Supporting Information

Chiral Phthalocyanines through Axial Coordination

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General Information

Materials

All the starting materials, reagents and solvents were purchased from commercial suppliers, unless otherwise specified, and used without further purification. Silicon phthalocyanine dichloride ($PcSi(Cl)_2$), L-phenylalanine and *N*,*N*-diisopropylethylamine (also known as Hünig's base), *N*-(tert-butoxycarbonyl)-L-isoleucine hemihydrate, (*S*)-(+)-2-(6-methoxy-2-naphtyl)propionic acid, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA), (*R*)-(+)-*N*-(1-phenylethyl)-succinamic acid and (*R*)-2-phenylpropionic acid were purchased from commercial sources (Sigma-Aldrich, TCI, Merck and Fluorochem). The reaction solvents (toluene and *N*,*N*-dimethylformamide) were supplied by VWR and Acros Organics, respectively. Samples for NMR spectroscopy were made up with $CDCl_3$ and $[D_6]$DMSO for NMI. UV-Vis, CD and fluorescence spectra were acquired in CH_2Cl_2.

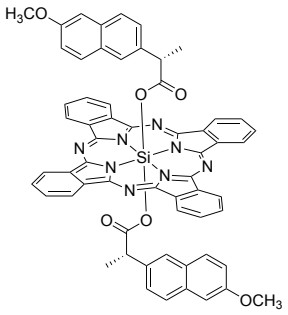
Instrumentation

All reactions were conducted in a CEM Discover microwave reactor using a sealed reaction vessel. ^1H and ^{13}C NMR spectra were acquired on a Agilent 500 spectrometer (^1H at 500 MHz and ^{13}C at 126 MHz) in $CDCl_3$ or $[D_6]$DMSO at 298 K. The chemical shifts (δ) were reported in parts per million (ppm), and ^1H NMR spectra were referenced to the residual solvent peak (δ = 7.26 ppm for $CDCl_3$ and δ = 2.50 ppm for $[D_6]$DMSO). ^{13}C NMR spectra were ^1H-decoupled and referenced to the residual solvent peak (δ = 77.0 ppm for $CDCl_3$, and δ = 39.43 ppm for $[D_6]$DMSO). The coupling constants (*J*) are reported in Hertz (Hz), and signal multiplicity is denoted as singlet (s), doublet (d), doublet of doublet (dd), doublet of doublet of doublets (ddd), triplet (t), doublet of triplets (dt), quartet (q), multiplet (m), and broad (b). The NSI spectra (positive mode) were recorded on a LTQ Orbitrap XL hybrid FTMS instrument. CD and UV-Vis experiments were performed on an Applied Photophysics Chirascan Circular Dichroism Spectrophotometer equipped with a Peltier Temperature Controller; all the experimental conditions and parameters are provided in the CD, absorbance and fluorescence analyses section. Fluorescence spectra were recorded on an Applied Photophysics Chirascan Circular Dichroism Spectrophotometer equipped with a CS / SEM accessory; all the experimental conditions and parameters are also provided in the CD, absorbance and fluorescence analyses section.

Synthesis

There have been other microwave-assisted syntheses published.[1,2] However, when applying these to the molecules reported in this manuscript, all these methods failed, thus we had to develop the following synthetic protocol.

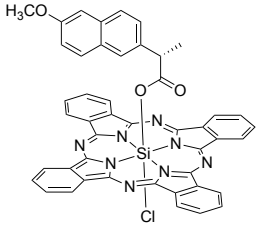
Synthesis of Pc1



$PcSi(Cl)_2$ (0.0292 g, 0.047 mmoles) was suspended in dry toluene (5 mL) in an 8-mL microwave tube. (*S*)-(+)-2-(6-methoxy-2-naphtyl) propionic acid (5 equiv, 0.0549 g, 0.238 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilize the reagents, and subsequently heated under microwave irradiation for 14 h at 155 °C. The solvent was removed under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water (3 x 50 mL). The solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromethane:ethyl acetate 9:1 v/v). The solvents were removed under reduced pressure to yield **Pc1** as a greenish-blue solid. Yield 68% (31.6 mg, 0.03196 mmoles). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.40 - 9.38 (m, 8H), 8.32 – 8.28 (m, 8H), 7.06 – 7.00 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 2.4 Hz, 2H), 6.50 (d, *J* = 8.2 Hz, 2H), 5.21 (s, 2H), 4.82 (dd, *J* = 8.3 Hz, 1.7 Hz, 2H), 4.09 (s, 6H), 0.55 (q, *J* = 6.9 Hz, 2H), -0.57 (d, *J* = 7.0 Hz, 6H).

Note: Full characterization of this molecule is provided in reference[3]

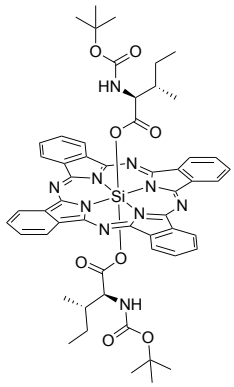
Synthesis of Pc2



$PcSi(Cl)_2$ (0.0292 g, 0.047 mmoles) was suspended in dry toluene (5 mL) in an 8-mL microwave tube. (*S*)-(+)-2-(6-methoxy-2-naphtyl) propionic acid (1 equiv, 0.0109 g, 0.047 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilize the reagents, and subsequently heated under microwave irradiation for 3 h at 125 °C. The solvent was removed under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water (3 x 50 mL). The solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromethane:ethyl acetate 8:2 v/v). The solvents were removed under reduced pressure to yield **Pc2** as a deep blue solid. Yield 15% (5.6 mg, 0.00705 mmoles). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.25 (dd, *J* = 17.9, 6.3 Hz, 8H), 8.28 – 8.22 (m, 8H), 7.00 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 5.18 (s, 1H), 4.78 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.06 (s, 3H), 0.48 (q, *J* = 7.1 Hz, 1H), -0.63 (d, *J* = 7.1 Hz, 3H). **TOF MS ASAP+**: *m/z* calcd for $C_{46}H_{29}ClN_8O_3Si$: 769.2132 [*M*-Cl]$^+$; found 769.1763.

Note: Due to low solubility of **Pc2** and its propensity toward aggregation, no ^{13}C NMR spectrum could be acquired in any solvent.

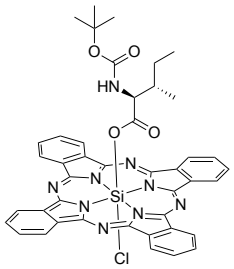
Synthesis of Pc3



$PcSi(Cl)_2$ (0.0289 g, 0.047 mmoles) was suspended in dry toluene (5 mL) in an 8-mL microwave tube. *N*-(tert-butoxycarbonyl)-L-isoleucine hemydrate (5 equiv, 0.0575 g, 0.239 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilize the reagents, and subsequently heated under microwave irradiation for 14 h at 155 °C. The solvent was removed under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water

(3 x 50 mL). The solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromethane:ethyl acetate 9:1 v/v). The solvents were removed under reduced pressure to yield **Pc3** as a greenish-blue solid. Yield 83% (39 mg, 0.03901 mmoles). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.76 – 9.66 (m, 8H), 8.45 – 8.36 (m, 8H), 3.18 (d, *J* = 8.1 Hz, 2H), 1.09 (dd, *J* = 8.2, 2.9 Hz, 2H), 0.83 (s, 18H), -0.36 (t, *J* = 7.3 Hz, 6H), -0.88 – -0.97 (m, 8H), -1.18 (dt, *J* = 14.8, 7.9 Hz, 2H), -1.86 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.7, 154.0, 150.2, 135.4, 134.2, 131.5, 124.0, 123.5, 78.2, 55.7, 35.8, 27.7, 22.4, 13.2, 10.4. **FTMS-pNSI**: *m/z* calcd for $C_{54}H_{56}N_{10}O_8Si$: 1001.4152 $[M+H]^+$; found 1001.4127.

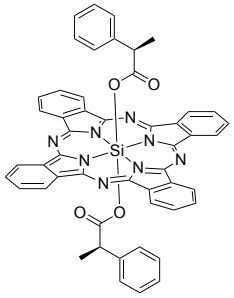
Synthesis of Pc4



$PcSi(Cl)_2$ (0.0292 g, 0.047 mmoles) was suspended in dry toluene (5 mL) in an 8 mL microwave tube. *N*-(tert-butoxycarbonyl)-L-isoleucine hemydrate (1 equiv, 0.0121 g, 0.050 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilize the reagents, and subsequently heated under microwave irradiation for 3 h at 125 °C. The solvent was removed under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water (3 x 50 mL). The solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromethane:ethyl acetate 9:1 v/v). The solvents were removed under reduced pressure to yield **Pc4** as a deep-blue solid. Yield 14% (5.3 mg, 0.00658 mmoles). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.40 – 9.25 (m, 8H), 8.35 – 8.20 (m, 8H), 3.03 (d, *J* = 8.2 Hz, 1H), 0.93 (t, *J* = 6.0 Hz, 1H), 0.75 (s, 9H), -0.54 (t, *J* = 7.3 Hz, 3H), -1.03 – -1.18 (m, 4H), -1.32 – -1.42 (m, 1H). **FTMS-pNSI**: *m/z* calcd for $C_{43}H_{36}ClN_9O_4Si$: 770.2654 $[M-Cl]^+$; found 770.2645.

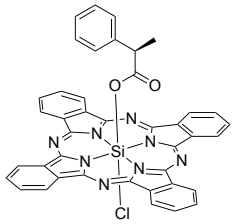
Note: Due to low solubility of **Pc4** and its propensity toward aggregation, no ^{13}C NMR spectrum could be acquired in any solvent.

Synthesis of Pc5



$PcSi(Cl)_2$ (0.029 g, 0.047 mmoles) was suspended in dry toluene (5 mL) in an 8-mL microwave tube. (*R*)-2-phenylpropionic acid (5 equiv, 0.0356 g, 0.237 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilize the reagents, and subsequently heated under microwave irradiation for 14 h at 155 °C. The solvent was reduced under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water (3 x 50 mL). The solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromethane:ethyl acetate 9:1 v/v). The solvents were removed under reduced pressure to yield **Pc5** as a greenish-blue solid. Yield 63% (21.6 mg, 0.02961 mmoles). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.61 (m, 8H), 8.37 (m, 8H), 6.60 (t, *J* = 7.2 Hz, 2H), 6.24 (t, *J* = 7.5 Hz, 4H), 4.79 (d, *J* = 7.5 Hz, 4H), 0.46 (q, *J* = 7.1 Hz, 2H), -0.64 (d, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 149.7, 138.9, 135.4, 130.9, 127.1, 125.5, 124.8, 123.9, 44.7, 15.3. **FTMS-pNSI**: *m/z* calcd for $C_{50}H_{34}N_8O_4Si$: 839.2545 $[M+H]^+$; found 839.2546.

Synthesis of Pc6

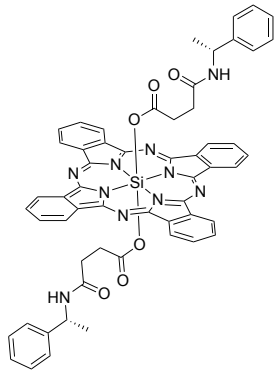


$PcSi(Cl)_2$ (0.029 g, 0.047 mmoles) was suspended in dry toluene (5 mL) in an 8-mL microwave tube. (*R*)-2-phenylpropionic acid (5 equiv, 0.0356 g, 0.237 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilize the reagents, and subsequently heated under microwave irradiation for 14 h at 155 °C. The solvent was removed under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water (3 x 50 mL). The

solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromethane:ethyl acetate 9:1 v/v). The solvents were removed under reduced pressure to yield **Pc5** as a deep-blue solid. Yield 6% (1.8 mg, 0.00282 mmoles). Note: **Pc6** has been isolated from the same reaction mixture as **Pc5**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.60 – 9.54 (brs, 8H), 8.34 (dd, *J* = 5.7, 2.9 Hz, 8H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.23 (t, *J* = 7.4 Hz, 2H), 4.77 (d, *J* = 7.5 Hz, 2H), -0.67 (d, *J* = 7.1 Hz, 3H). **MALDI+**: *m/z* calcd for $C_{41}H_{25}ClN_9O_4Si$: 770.2654 $[M\text{-Cl}]^+$; found 770.2645.

Note: Due to low solubility of **Pc6** and its propensity toward aggregation, no ^{13}C NMR spectrum could be acquired in any solvent.

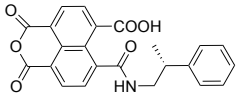
Synthesis of Pc7



$PcSi(Cl)_2$ (0.0294 g, 0.048 mmoles) was suspended in dry toluene (5 mL) in an 8-mL microwave tube. (*R*)-(+)-*N*-(1-phenylethyl)-succinamic acid (5 equiv, 0.0505 g, 0.228 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilize the reagents, and subsequently heated under microwave irradiation for 14 h at 155 °C. The solvent was removed under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water (3 x 50 mL). The solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromethane:ethyl acetate 9:1 v/v). Two other conformationally different di-substituted derivatives have isolated from the reaction mixture in dichloromethane:ethyl acetate 8:2 v/v. These were obtained in very low yields, and, providing that their CD / UV-Vis properties are identical to the main isolated species, they were not separately discussed. The solvents were removed under reduced pressure to yield **Pc7** as a greenish-blue solid. Yield 33% (15.5 mg, 0.01584 mmoles). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.85 – 9.56 (m, 8H), 8.38 (m,

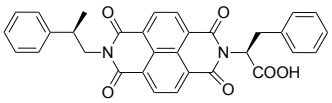
8H), 7.12 (d, *J* = 6.0 Hz, 4H), 6.66 (d, *J* = 4.9 Hz, 4H), 4.72 (d, *J* = 7.9 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 0.66 (d, *J* = 6.9 Hz, 6H), 0.37 (t, *J* = 6.9 Hz, 4H), -0.46 (t, *J* = 6.9 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 166.6, 150.0, 142.9, 135.5, 131.4, 128.8, 128.3, 126.8, 125.6, 124.0, 47.8, 29.8, 21.1. **FTMS-pNSI**: *m/z* calcd for $C_{56}H_{44}N_{10}O_6Si$: 981.3287 $[M\text{-}H]^+$; found 981.3289.

Synthesis of NMI[4]



1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA; 200 mg, 0.75 mmoles) and Et_3N (0.25 mL) were suspended in DMF (5 mL) in an 8-mL microwave tube, and then cooled on an ice bath while stirring. (*S*)-β-methylphenetylamine (0.5 equiv, 59 μL, 0.375 mmoles) was added in one go and stirred in ice for 15 min. Subsequently, (*S*)-β-methylphenetylamine (0.5 equiv, 59 μL, 0.375 mmoles) was added dropwise to the reaction mixture and stirred for 45 min until it became homogeneous. The ice bath was removed, and the reaction mixture was allowed to warm to room temperature under stirring, followed by heating under microwave irradiation for 10 min at 125 °C. The solvent was removed under reduced pressure, and the crude residue was dissolved in the minimum volume of acetone followed by precipitation in vigorously stirred 1 M HCl_{aq}. The suspension was filtered off and the precipitate collected and dried under vacuum to yield the **NMI** as a pale-yellow solid. Yield 75% (226.3 mg, 0.56 mmoles). **^{1}H NMR** (500 MHz, $[D_6]$DMSO): δ 13.38 (s, 1H), 8.96 (t, *J* = 5.7 Hz, 1H), 8.53 (d, *J* = 4.5 Hz, 1H), 8.52 (d, *J* = 4.5 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.18 (m, 5H), 3.45 (dt, *J* = 12.7, 6.2 Hz, 1H), 3.15 – 3.06 (m, 1H), 1.29 (d, *J* = 7.0 Hz, 3H). One of the protons was masked by the water peak. **^{13}C NMR** (126 MHz, $[D_6]$DMSO) δ 168.4, 168.4, 162.7, 160.6, 160.6, 145.4, 141.4, 132.1, 131.9, 131.2, 129.2, 128.8, 128.5, 127.6, 126.7, 125.7, 121.9, 121.2, 46.9, 39.2, 36.2, 31.2, 19.9.

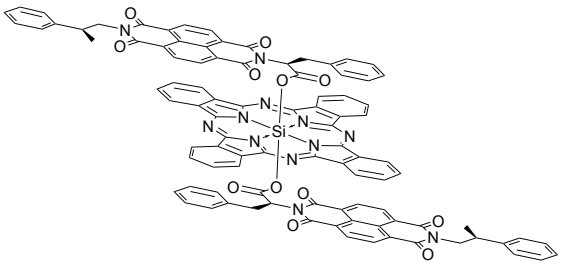
Synthesis of NDI



NMI previously synthesized (100 mg, 0.247 mmoles) and L-phenylalanine (1.1 equiv, 45.04 mg, 0.272 mmoles) were suspended in DMF (5 mL) in an 8-mL microwave tube, and Et_3N (0.25 mL) added. The reaction mixture was sonicated until it became homogeneous, and subsequently heated under microwave irradiation for 10 min at 125 °C. The solvent was removed under reduced pressure, and the crude residue was dissolved in the minimum volume of ace-

tone followed by precipitation in vigorously stirred 1 M HCl_{aq}. The suspension was filtered off and the precipitate collected ^{1}H NMR analysis of the product revealed two NDI-based products. Purification by column chromatography with dichloromethane:ethyl acetate 9:1 allowed the isolation of the desired product. The solvents were removed under reduced pressure, and the residue dried under vacuum to yield the **NDI** as yellow solid. Yield 33% (33 mg, 0.062 mmoles). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.67, 8.65 (2d, *J* = 7.6 Hz, 4H), 7.34 – 7.01 (m, 10H), 6.08 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.41 – 4.31 (m, 2H), 3.70 (dd, *J* = 14.4, 5.6 Hz, 1H), 3.50 (dd, *J* = 14.3, 10.1 Hz, 1H), 3.42 (sext, *J* = 7.3 Hz, 1H), 1.34 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 174.30, 162.77, 162.28, 143.36, 136.56, 131.35, 130.95, 129.08, 128.42, 128.39, 127.40, 126.82, 126.71, 126.65, 126.58, 125.77, 77.20, 54.43, 47.23, 38.06, 34.59, 29.68, 18.65. **FTMS-pNSI**: *m/z* calcd for $C_{32}H_{24}N_2O_6$: 533.1707 $[M\text{-H}]^+$; found 533.1702.

Synthesis of Pc8

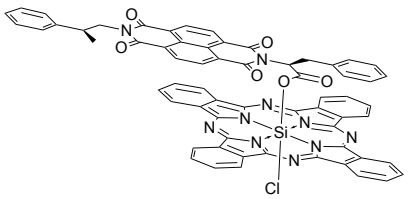


$PcSi(Cl)_2$ (0.0072 g, 0.012 mmoles) was suspended in dry toluene (5 mL) in an 8 mL microwave tube. **De-symmetrised NDI** previously synthesized (5 equiv, 0.033 g, 0.062 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilize the reagents, and subsequently heated under microwave irradiation for 14 h at 155 °C. The solvent was removed under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water (3 x 50 mL). The solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromenthane). The solvent was removed under reduced pressure to yield **Pc8** as a greenish-blue solid. Yield 42% (8.08 mg, 0.00504 mmoles). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.21 – 9.16 (m, 8H), 8.39 (d, *J* = 7.4 Hz, 4H), 8.21 – 8.15 (m, 8H), 7.54 (d, *J* = 8.0 Hz, 4H), 7.49 (d, *J* = 7.4 Hz, 4H), 7.45 (t, *J* = 8.0 Hz, 4H), 7.33 (d, *J* = 7.3 Hz, 2H), 6.48 (t, *J* = 7.3 Hz, 2H), 6.42 (t, *J* = 7.3 Hz, 4H), 5.90 (d, *J* = 8.0 Hz, 4H), 4.67 (dd, *J* = 13.4, 8.1 Hz, 2H), 4.52 (dd, *J* = 13.4, 8.1 Hz, 2H), 3.71 (sext, *J* = 7.4 Hz, 2H), 2.86 (dd, *J* = 11.3, 4.7 Hz,

2H), 1.61 (dd, *J* = 15.4, 4.7 Hz, 2H), 1.58 – 1.53 (6H*), 1.52 – 1.48 (dd, *J* = 15.4, 4.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 163.03, 160.90, 159.71, 149.53, 143.59, 136.50, 134.87, 131.05, 130.52, 129.86, 128.65, 127.68, 127.57, 127.50, 126.99, 125.94, 125.84, 125.61, 124.27, 123.65, 77.19, 53.10, 47.22, 38.42, 31.53, 29.68, 19.34. **FTMS-pNSI**: *m/z* calcd for $C_{96}H_{62}O_{12}N_{12}Si$: 1604.4481 $[M+H]^+$; found 1604.4472.

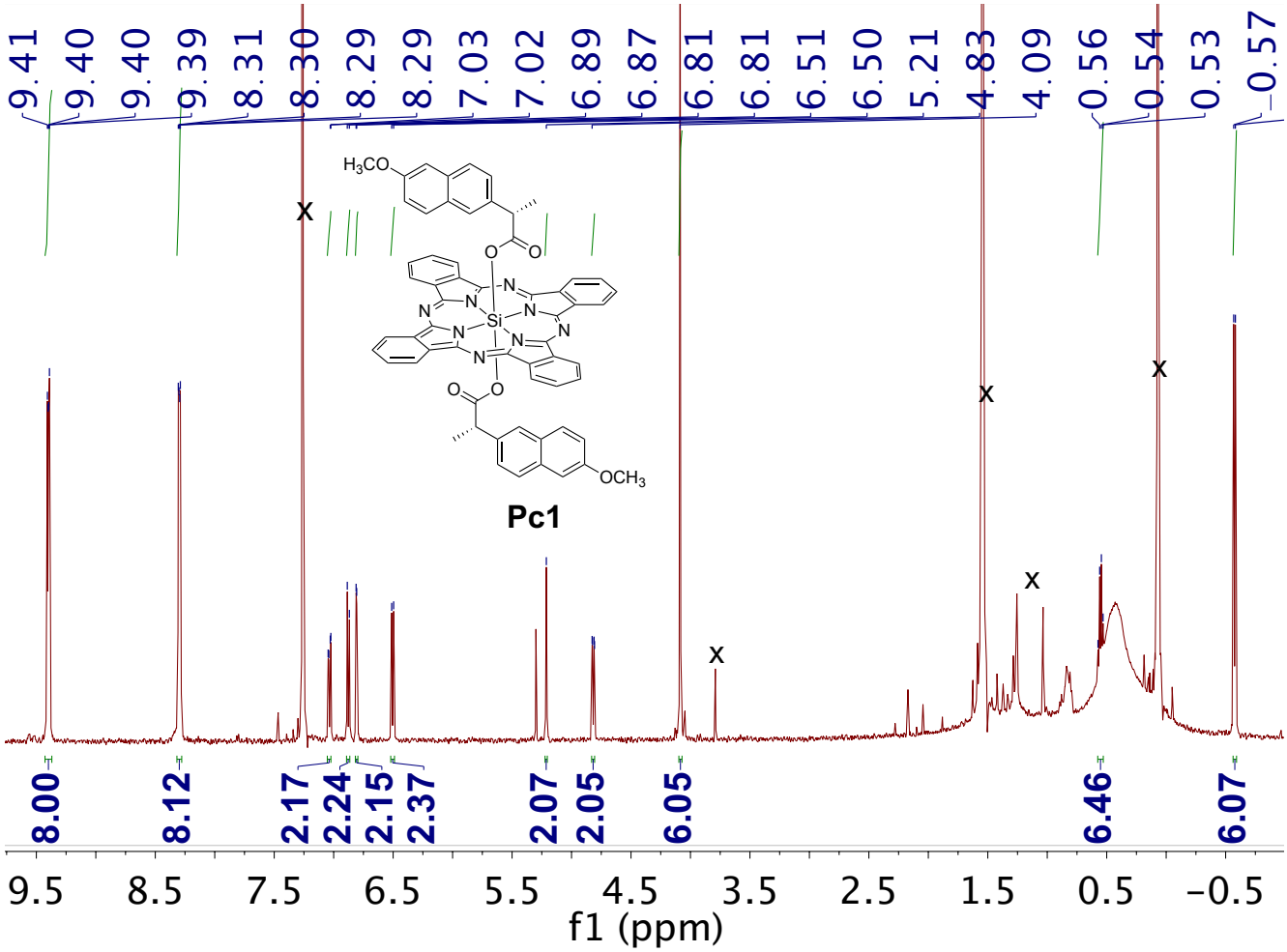
* The chemical shift and multiplicity could not by determined due to the water peak.

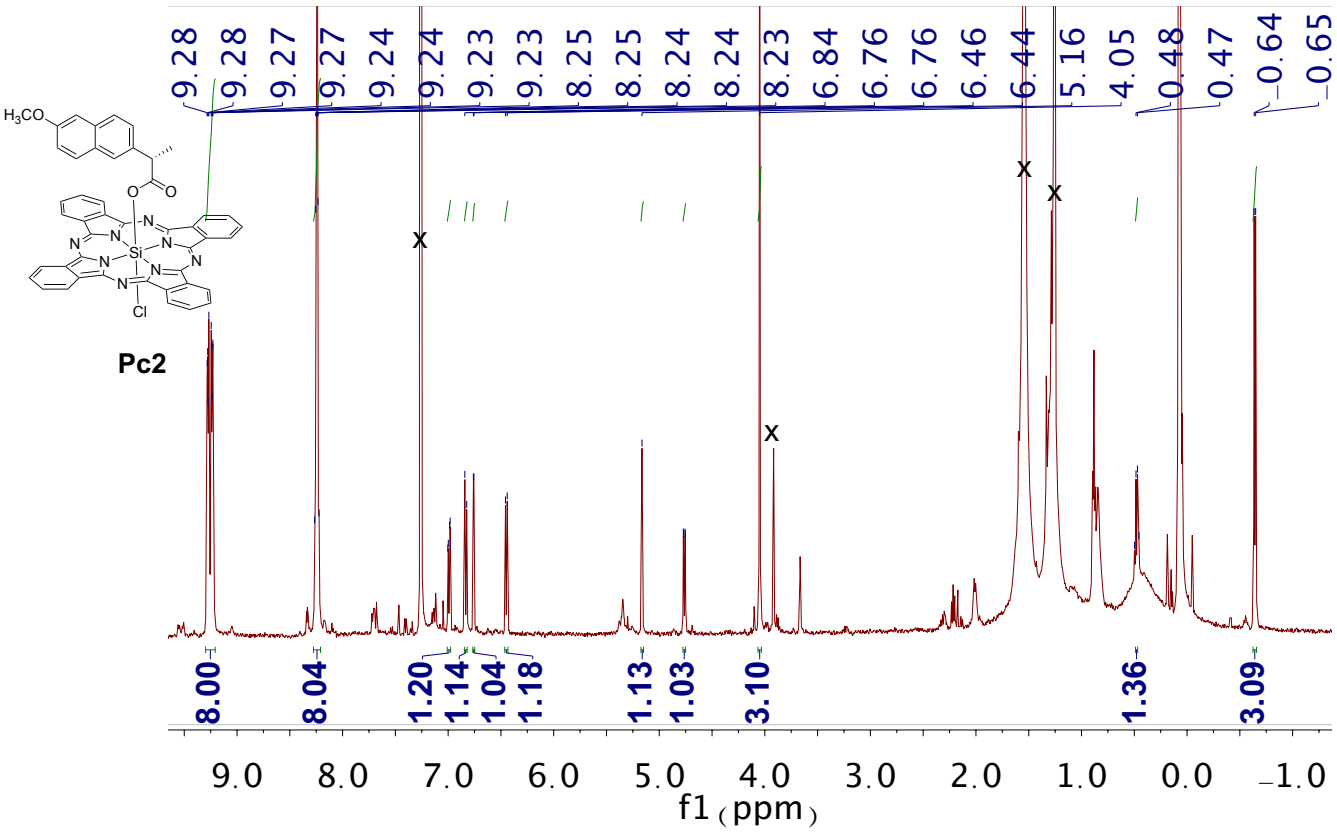
Synthesis of Pc9



$PcSi(Cl)_2$ (0.0072 g, 0.012 mmoles) was suspended in dry toluene (5 mL) in an 8-mL microwave tube. **NDI** previously synthesized (5 equiv, 0.033 g, 0.062 mmoles) and dry Hünig's base (0.5 mL) were added to the reaction mixture. This was sonicated for a few seconds to fully solubilise the reagents, and subsequently heated under microwave irradiation for 14 h at 155 °C. The solvent was removed under reduced pressure to yield a blue solid which was further collected in ethyl acetate. The residue was filtered off to remove any unreacted starting material, and the filtrate was washed with $NaHCO_{3(sat.)}$ (3 x 50 mL) and water (3 x 50 mL). The solvent was removed under reduced pressure, and NMR spectroscopy revealed a mixture of di- and mono-substituted derivatives. The mixture was separated on column chromatography (dichloromenthane:ethyl acetate 9:1). The solvent was removed under reduced pressure to yield **Pc8** as a greenish-blue solid. Yield 51% (6.77025 mg, 0.00612 mmoles). Note: **Pc9** has been isolated from the same reaction mixture as **Pc8**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.11 – 8.89 (m, 8H), 8.33-8.20 (brs, 2H), 8.20 – 8.06 (m, 8H), 7.56 – 7.33 (m, 7H), 6.44 (t, *J* = 7.2 Hz, 1H), 6.37 (t, *J* = 7.5 Hz, 2H), 5.85 (d, *J* = 7.8 Hz, 2H), 4.64 (ddd, *J* = 20.7, 13.6, 8.2 Hz, 1H), 4.47 (td, *J* = 13.3, 8.0 Hz, 1H), 3.68 (dt, *J* = 13.3, 7.3 Hz, 1H), 2.75 – 2.70 (m, 1H), 1.51 – 1.46 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.05, 149.17, 136.73, 134.93, 130.80, 130.44, 128.62, 127.73, 127.51, 127.39, 125.68, 125.43, 124.29, 123.40, 53.13, 47.13, 38.34, 31.41, 29.68, 29.34, 22.68, 19.36, 14.10. **MALDI+**: *m/z* calcd for $C_{41}H_{25}ClN_8O_2Si$: 540.1 $[M\text{-Cl-}C_9H_9O_8]^+$; found 540.5.

All the relevant NMR spectra (^{1}H, ^{13}C where possible, and COSY where necessary) are provided in the following pages in the order they appear in the Synthesis Section. All the peaks coming from solvents and impurities (mostly coming from the dirty probe within the NMR instrument) have been labelled with an “x”.




Pc2
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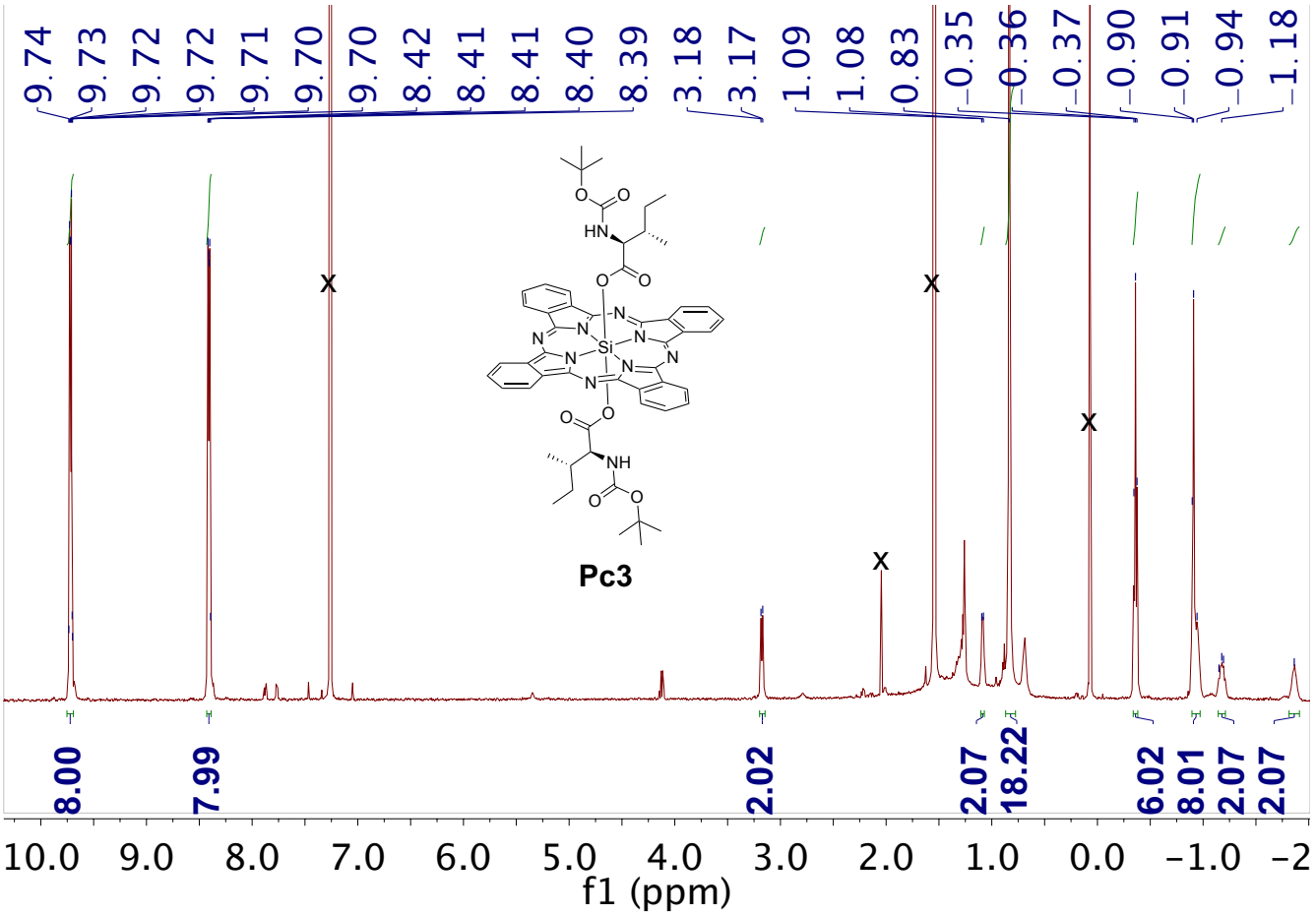
8.00 8.04 1.20 1.14 1.04 1.18 1.13 1.03 3.10 1.36 3.09
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0
f1 (ppm)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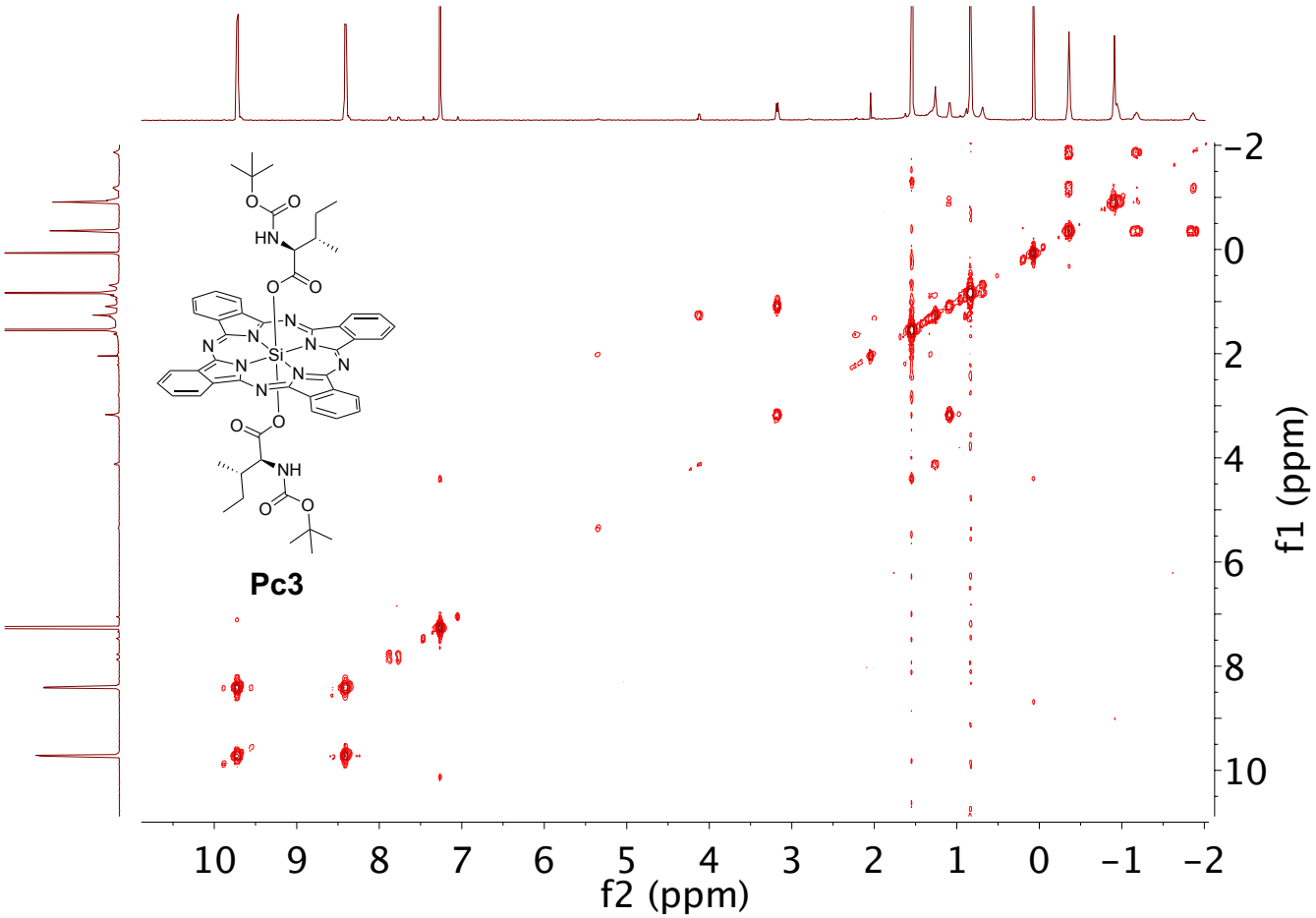
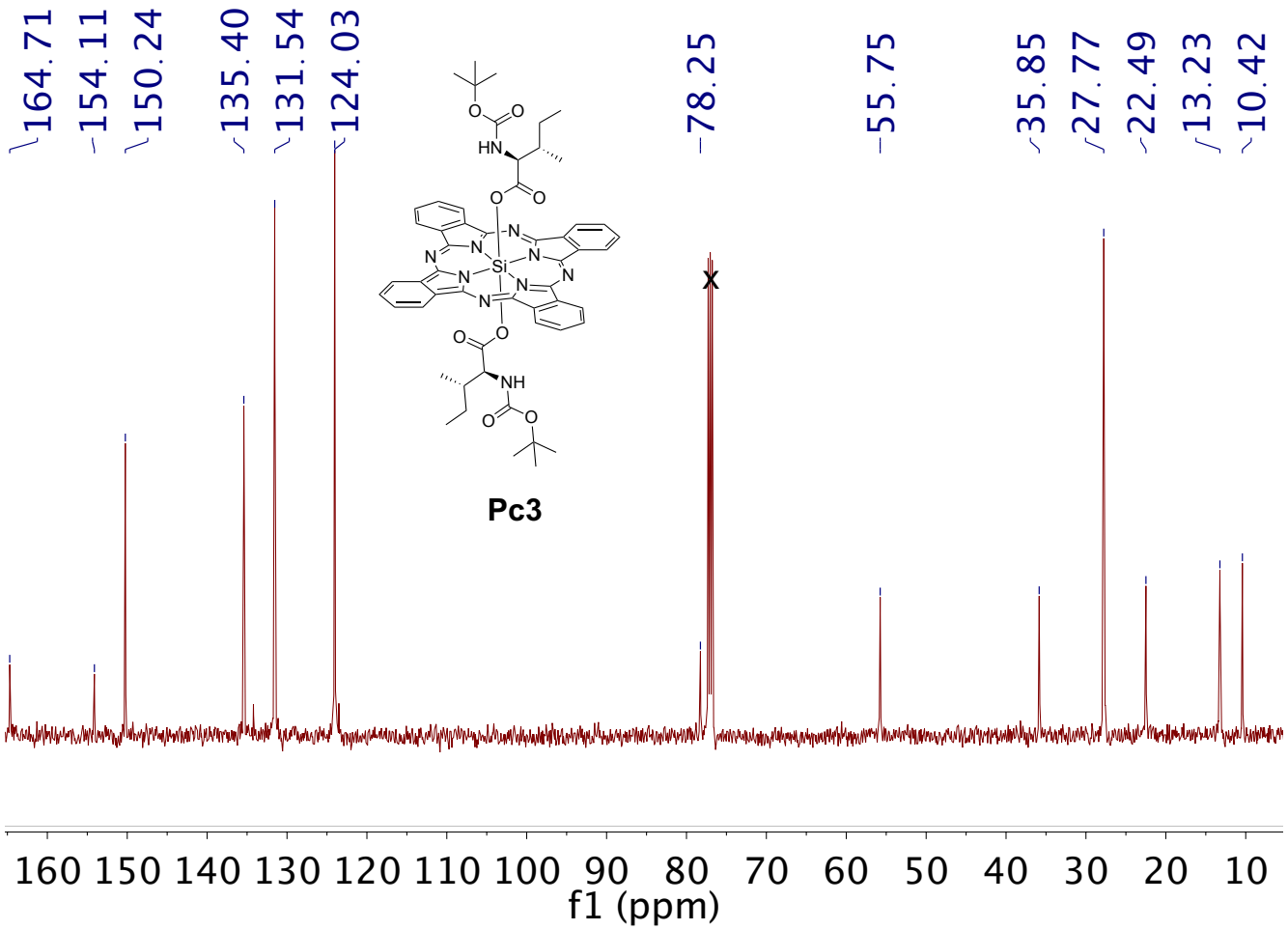
8.00 7.99 2.02 2.07 18.22 6.02 8.01 2.07 2.07
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0 −2
f1 (ppm)


Pc3
f2 (ppm)
f1 (ppm)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154.11
150.24
135.40
131.54
124.03
78.25
55.75
35.85
27.77
22.49
13.23
10.42
X
Pc3
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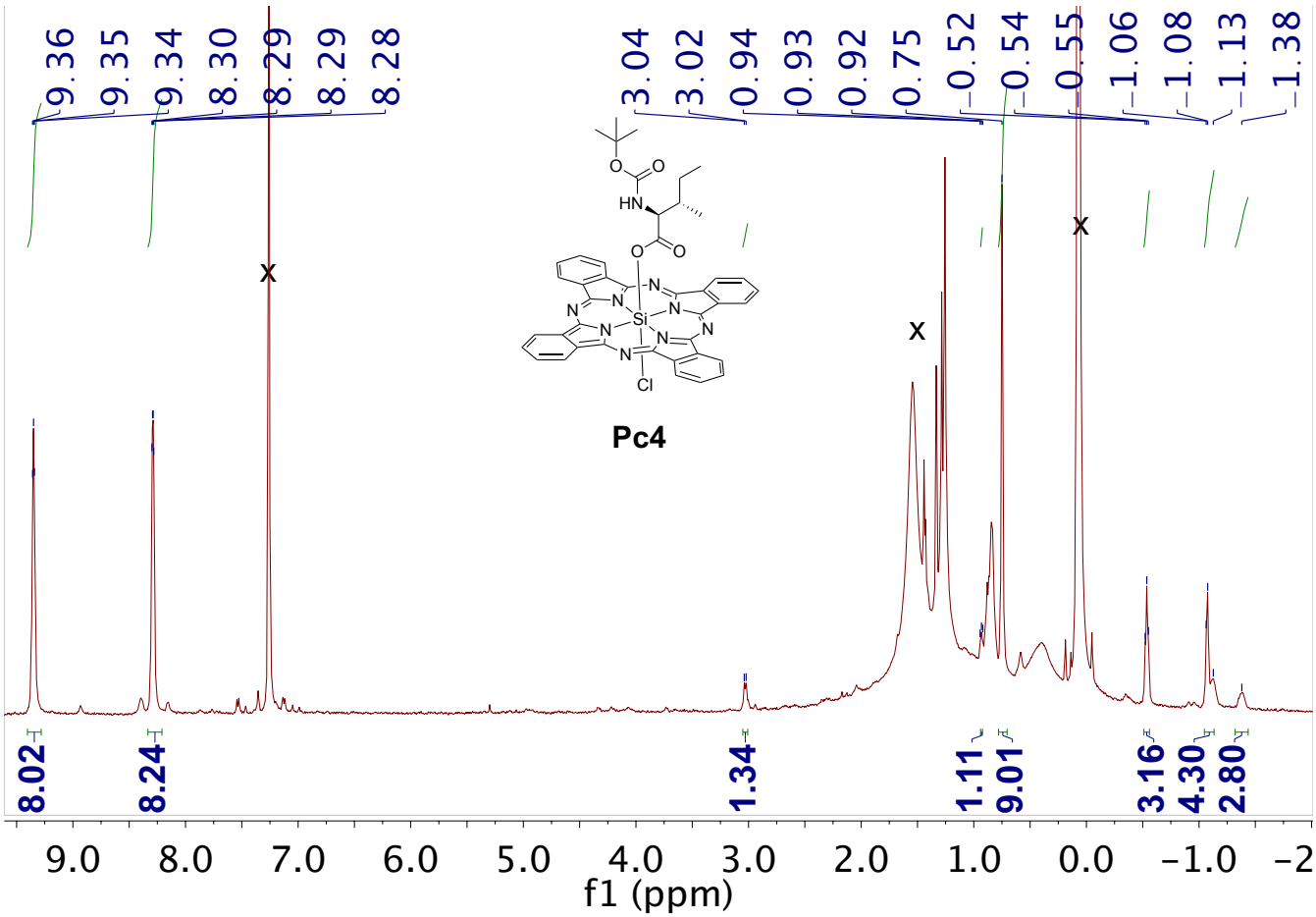
f1 (ppm)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9.35
9.34
8.30
8.29
8.29
8.28
3.04
3.02
0.94
0.93
0.92
0.75
0.52
0.54
0.55
1.06
1.08
1.13
1.38
Pc4
8.02
8.24
1.34
1.11
9.01
3.16
4.30
2.80
9.0
8.0
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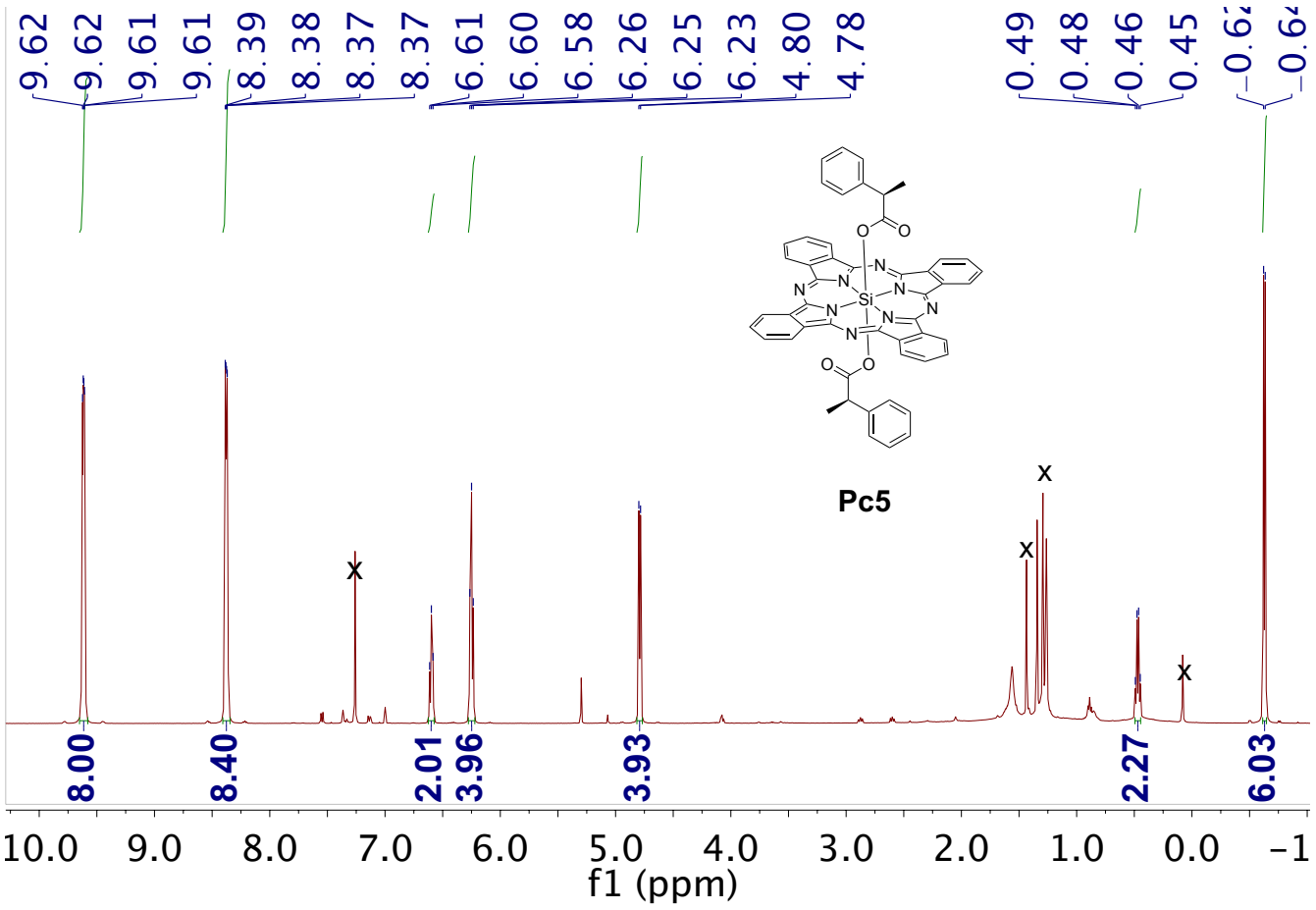
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
−2
f1 (ppm)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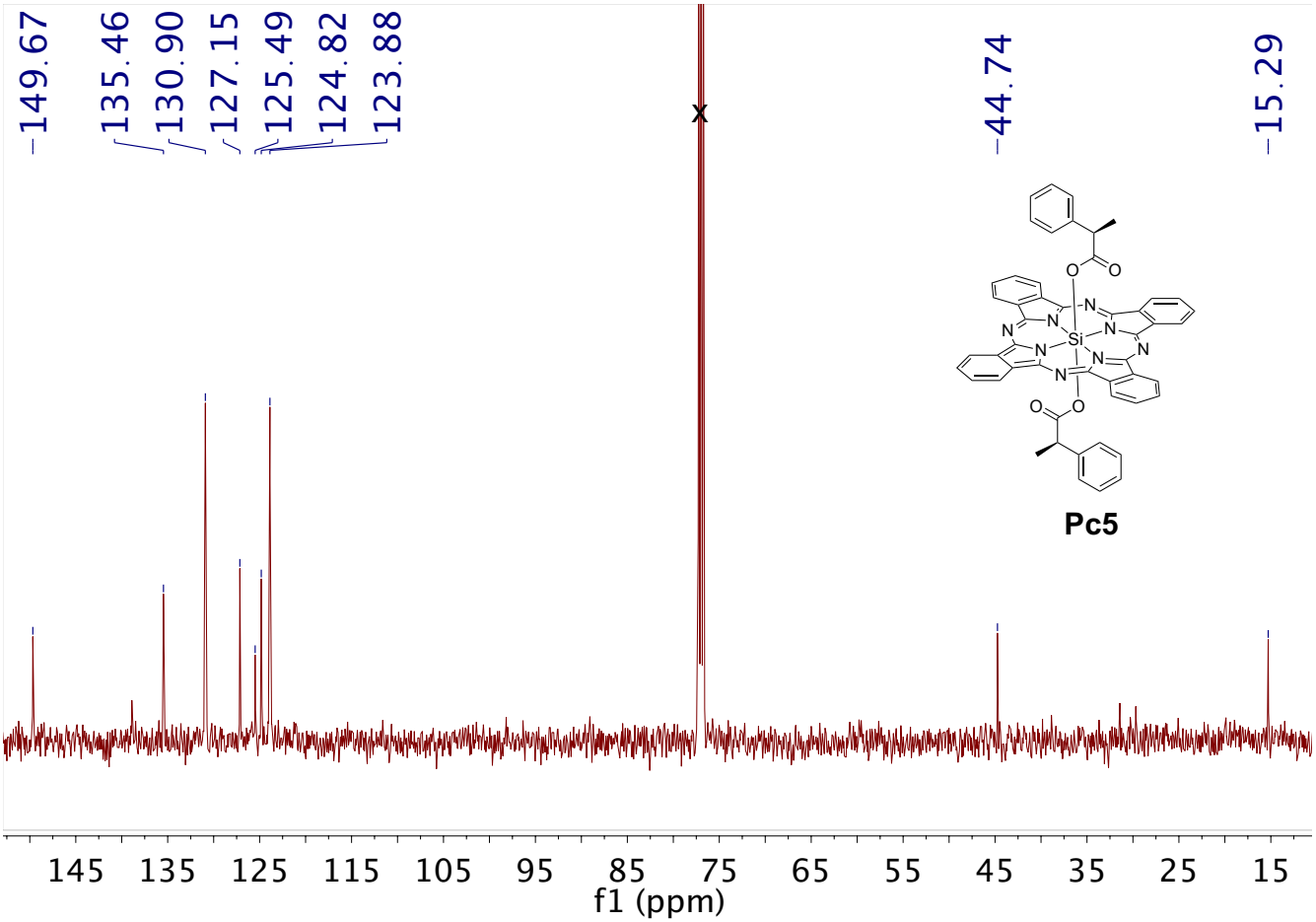
9.62
9.61
9.61
8.39
8.38
8.37
8.37
6.61
6.60
6.58
6.26
6.25
6.23
4.80
4.78
0.49
0.48
0.46
0.45
Pc5
8.00
8.40
2.01
3.96
3.93
2.27
6.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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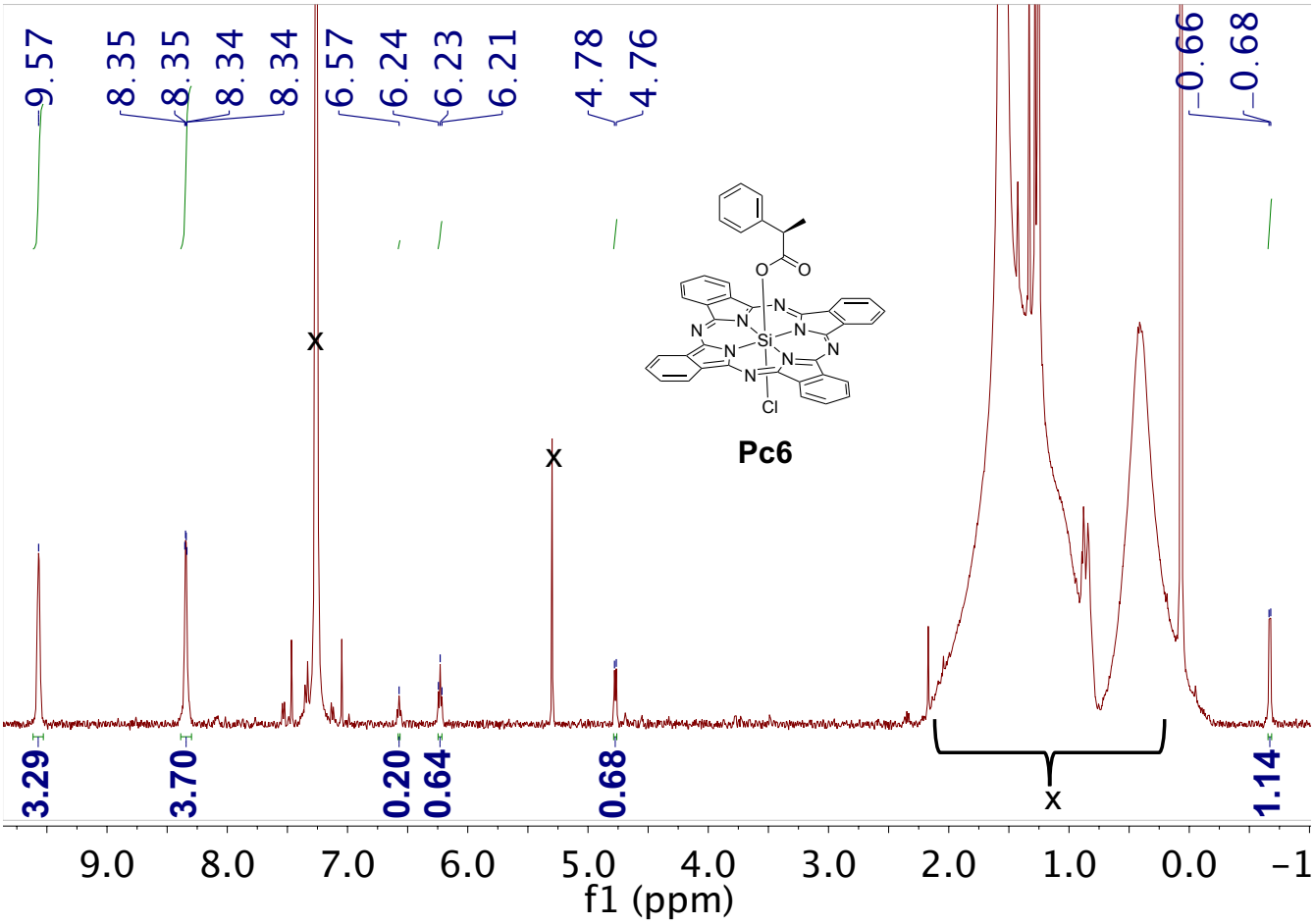
135.46
130.90
127.15
125.49
124.82
123.88
44.74
15.29
Pc5
145 135 125 115 105 95 85 75 65 55 45 35 25 15
f1 (ppm)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8.34
8.34
6.57
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6.23
6.21
4.78
4.76
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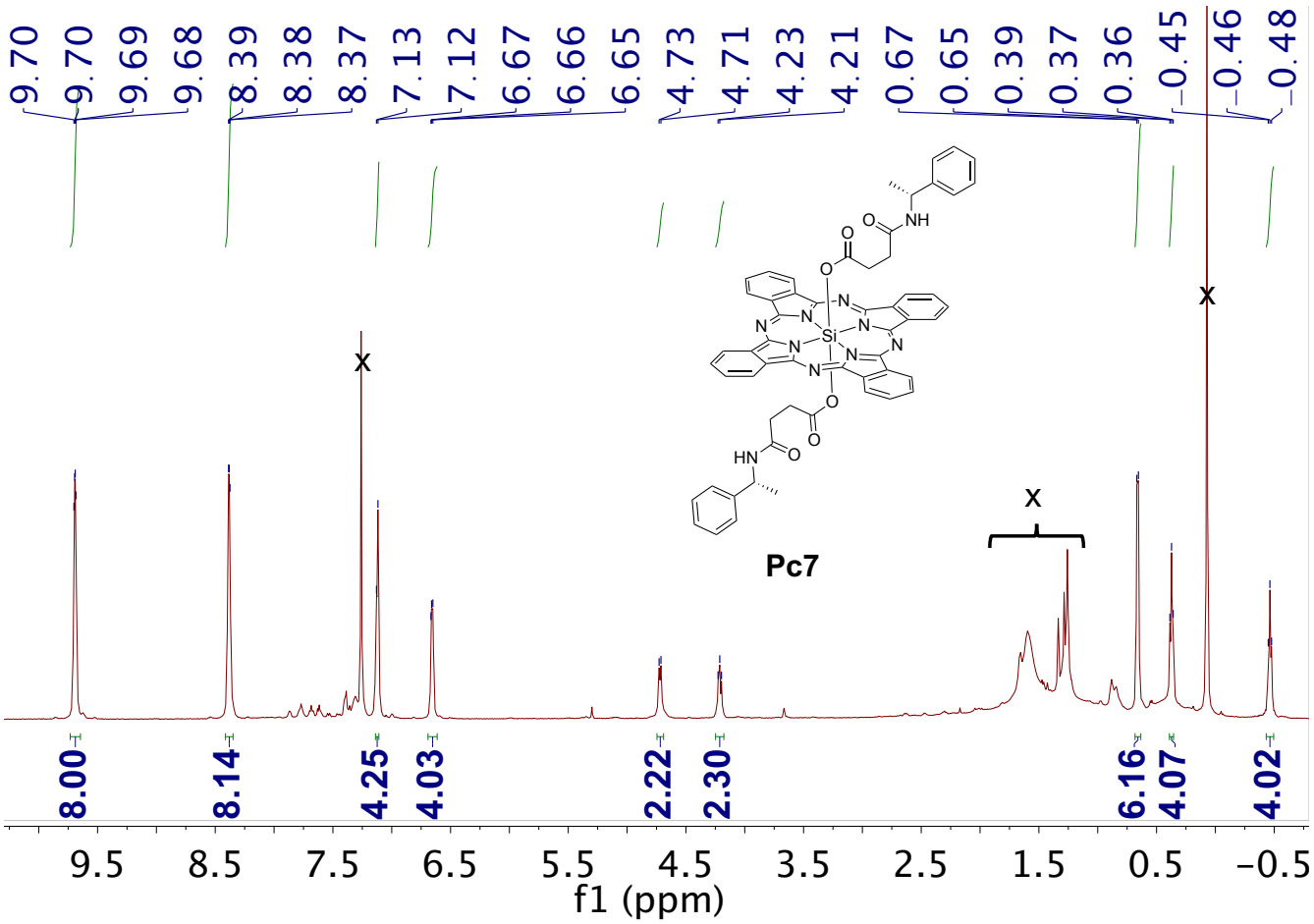
0.68
Pc6
3.29
3.70
0.20
0.64
0.68
1.14
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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9.70
9.69
9.68
8.39
8.38
8.37
7.13
7.12
6.67
6.66
6.65
4.73
4.71
4.23
4.21
0.67
0.65
0.39
0.37
0.36
-0.45
-0.46
-0.48
X
X
X
Pc7
8.00
8.14
4.25
4.03
2.22
2.30
6.16
4.07
4.02
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
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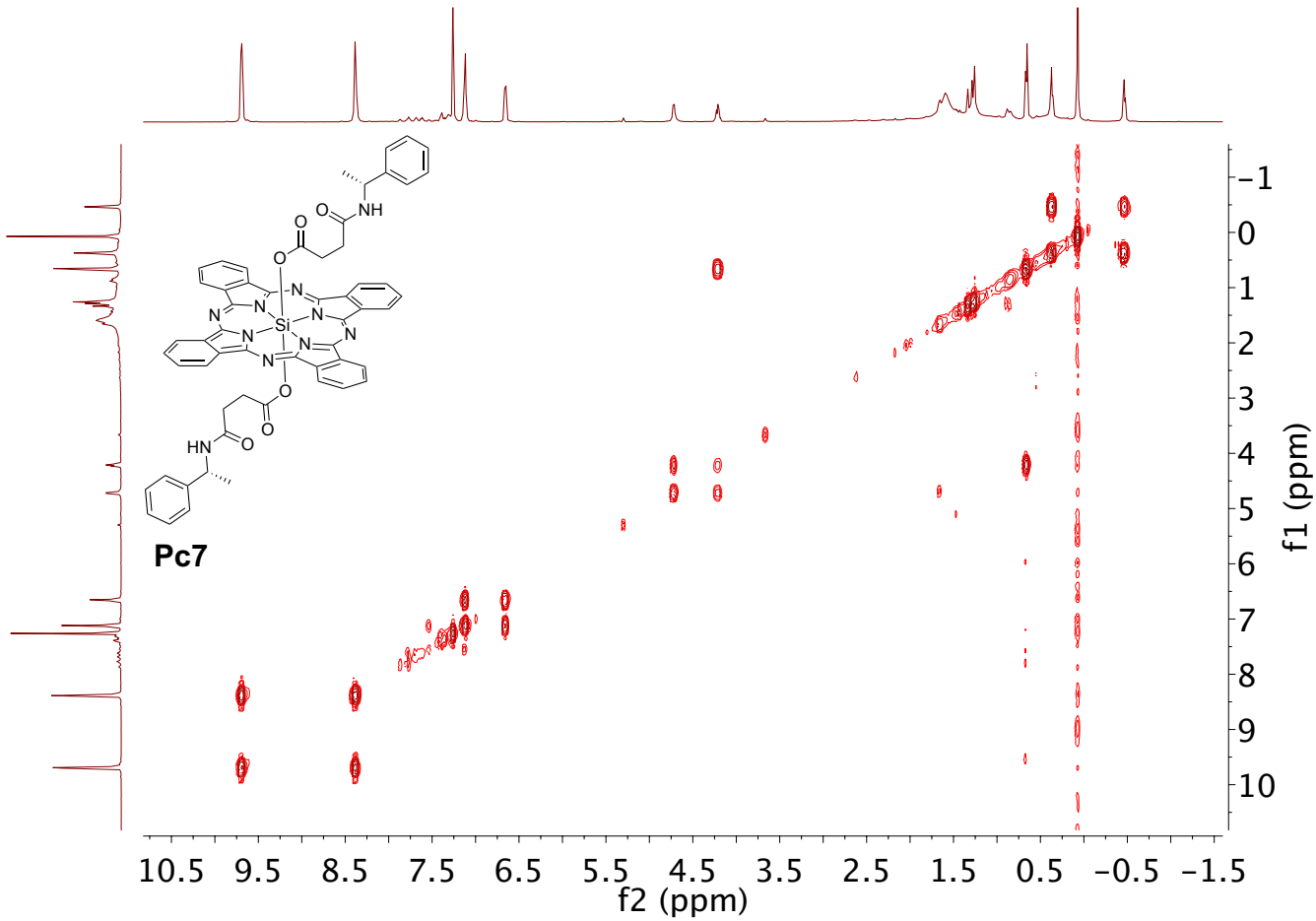
-0.5
f1 (ppm)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2.5
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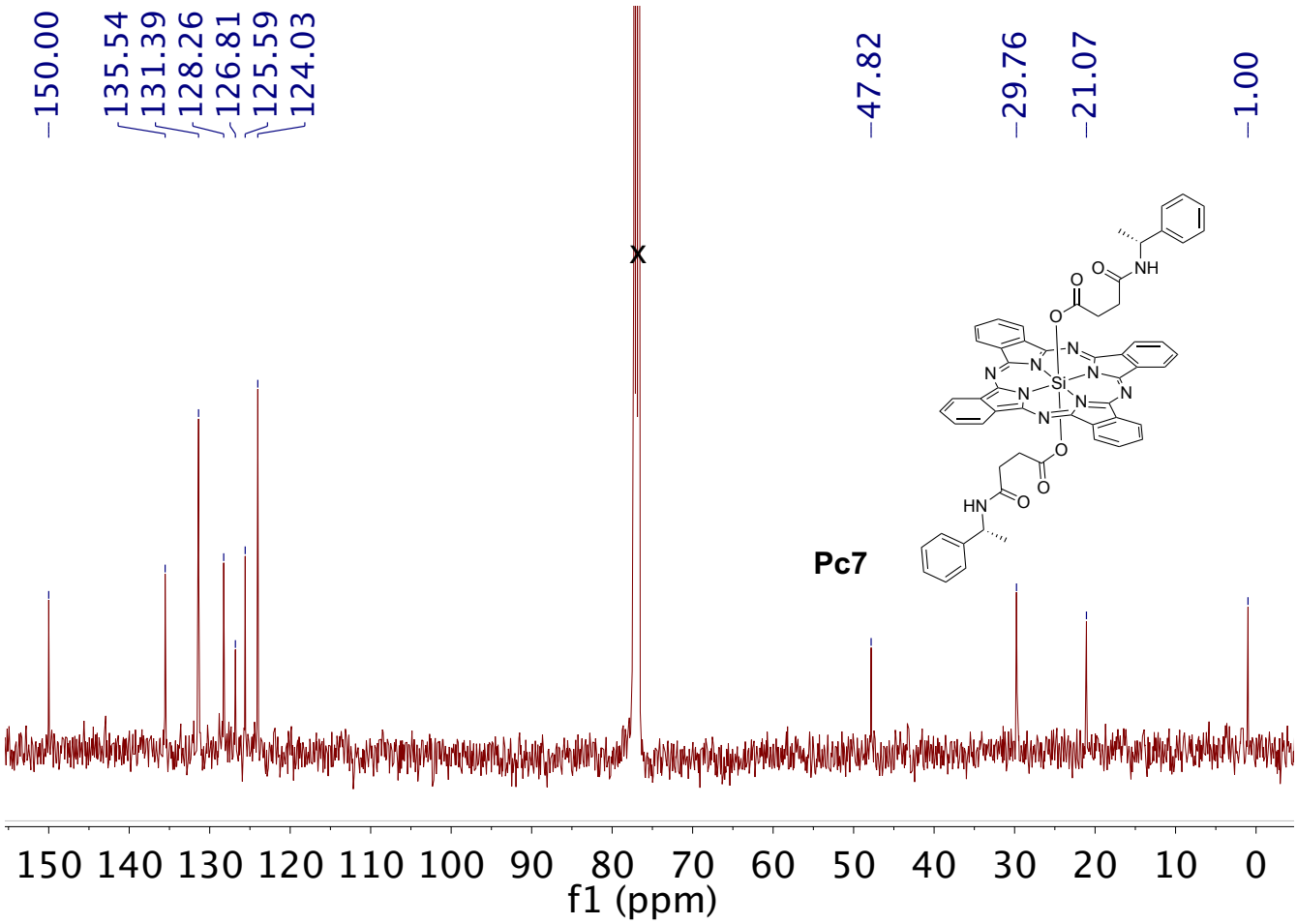
-1.5
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
9
10
f1 (ppm)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21.07
1.00
X
Pc7
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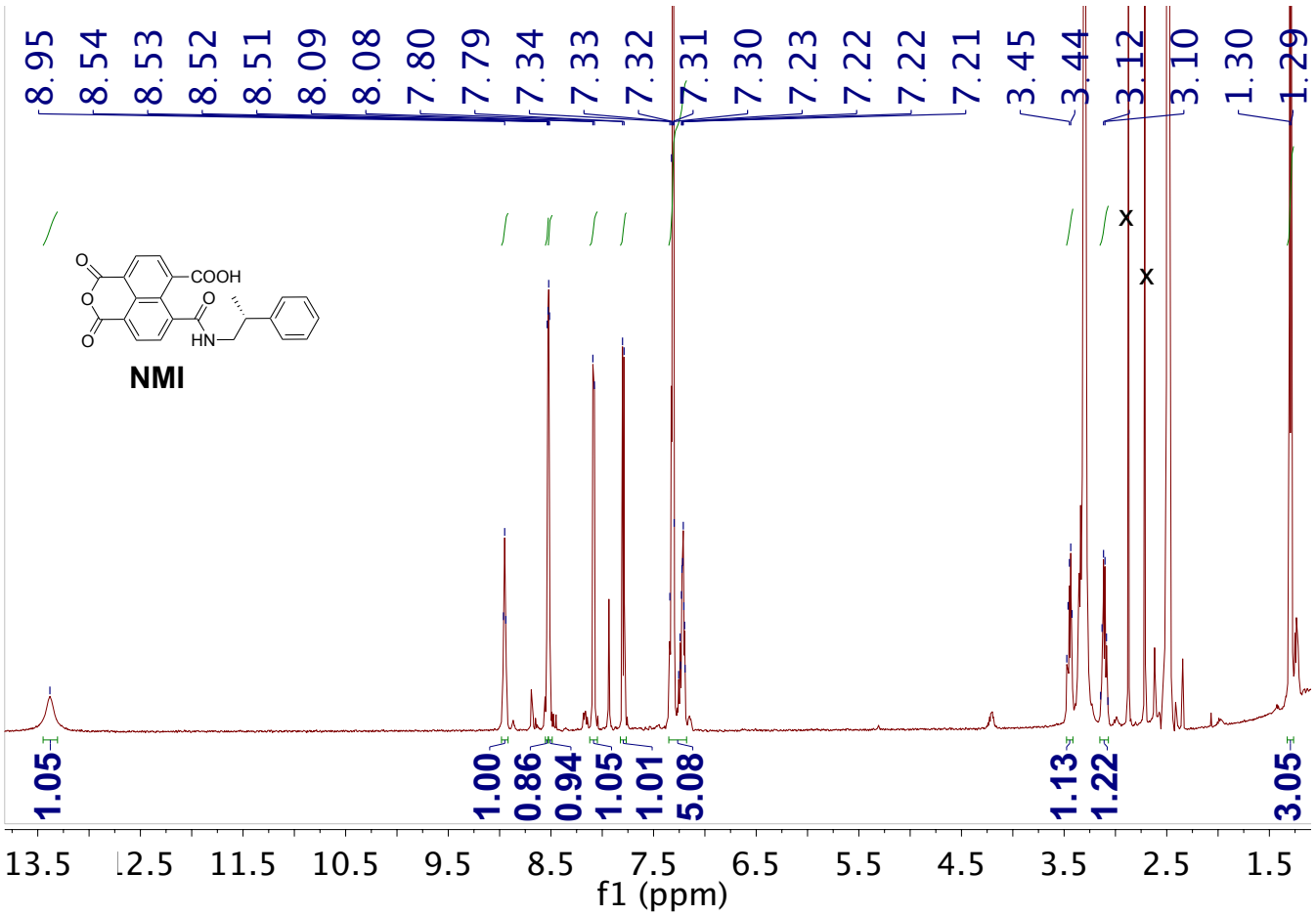
f1 (ppm)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7.31
7.30
7.23
7.22
7.22
7.21
3.45
3.44
3.12
3.10
1.30
1.29
COOH
O
O
O
O
HN
NMI
X
X
1.05
1.00
0.86
0.94
1.05
1.01
5.08
1.13
1.22
3.05
13.5
12.5
11.5
10.5
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8.5
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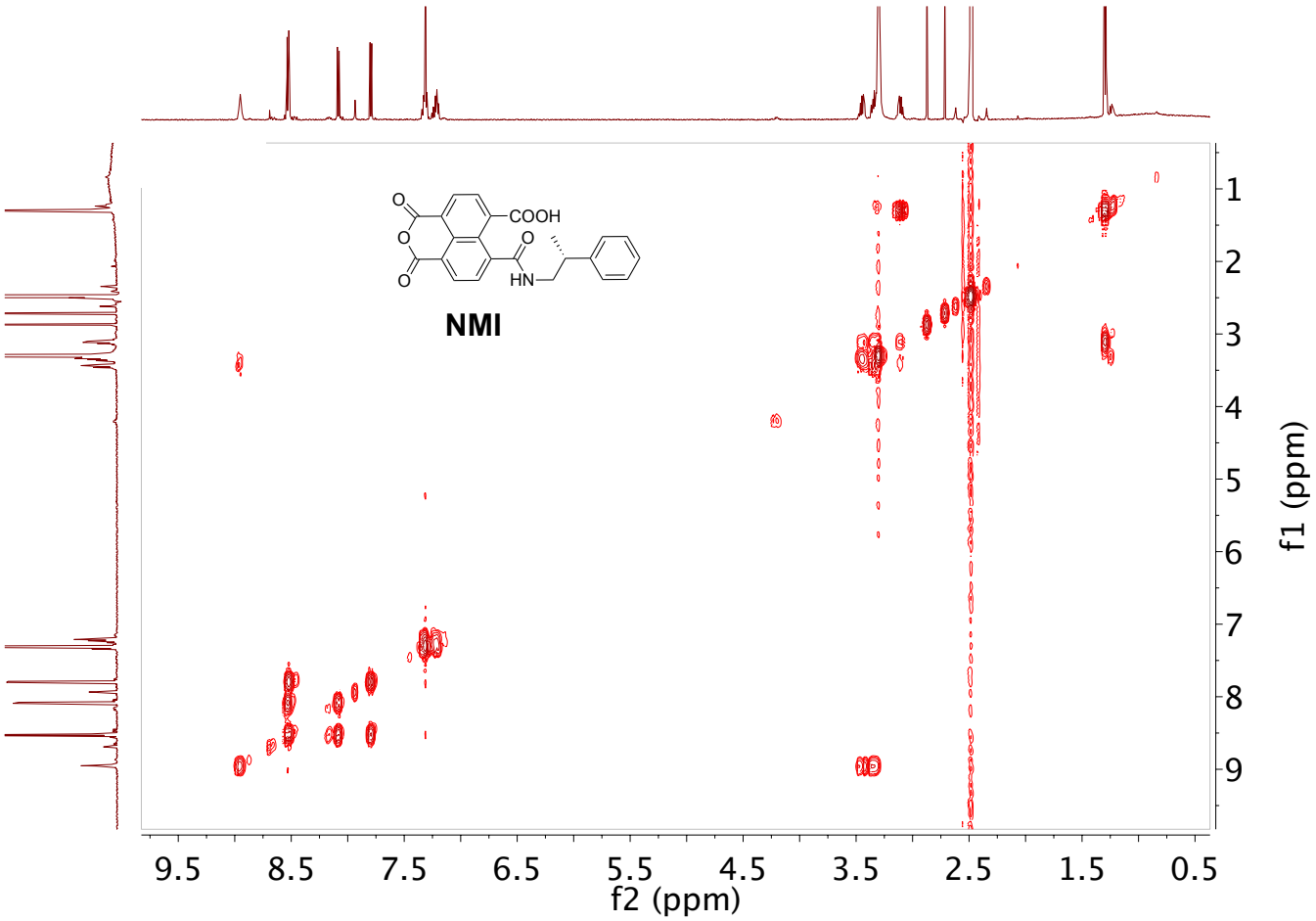
4.5
3.5
2.5
1.5
f1 (ppm)


COOH
O
O
O
O
HN
NMI
f2 (ppm)
f1 (ppm)
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8.5
7.5
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3.5
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1.5
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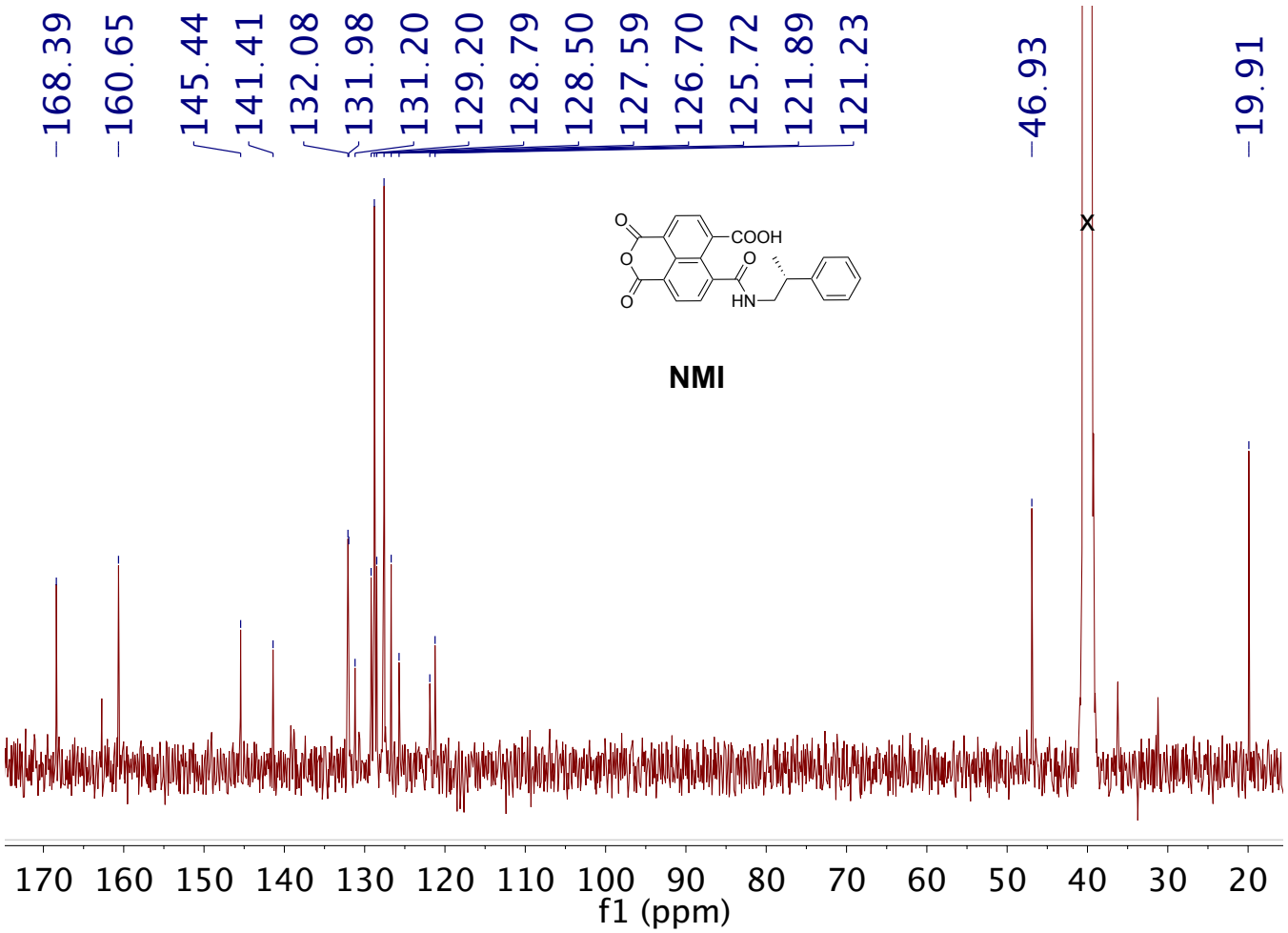
1
2
3
4
5
6
7
8
9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131.20
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128.50
127.59
126.70
125.72
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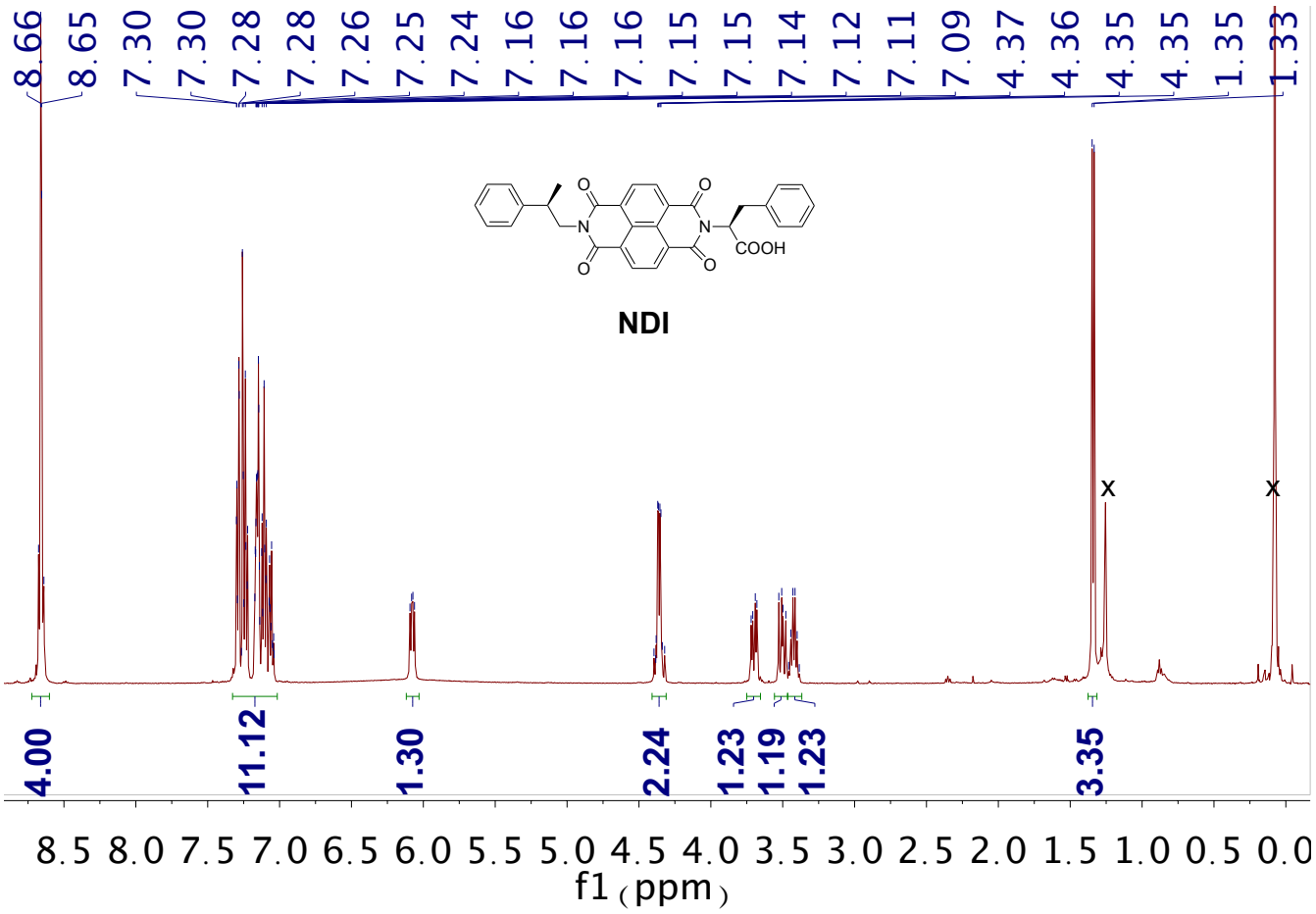
121.23
46.93
19.91
COOH
O
HN
NMI
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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7.24
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7.16
7.16
7.15
7.15
7.14
7.12
7.11
7.09
4.37
4.36
4.35
4.35
1.35
1.33
O
O
N
N
O
O
COOH
NDI
X
X
4.00
11.12
1.30
2.24
1.23
1.19
1.23
3.35
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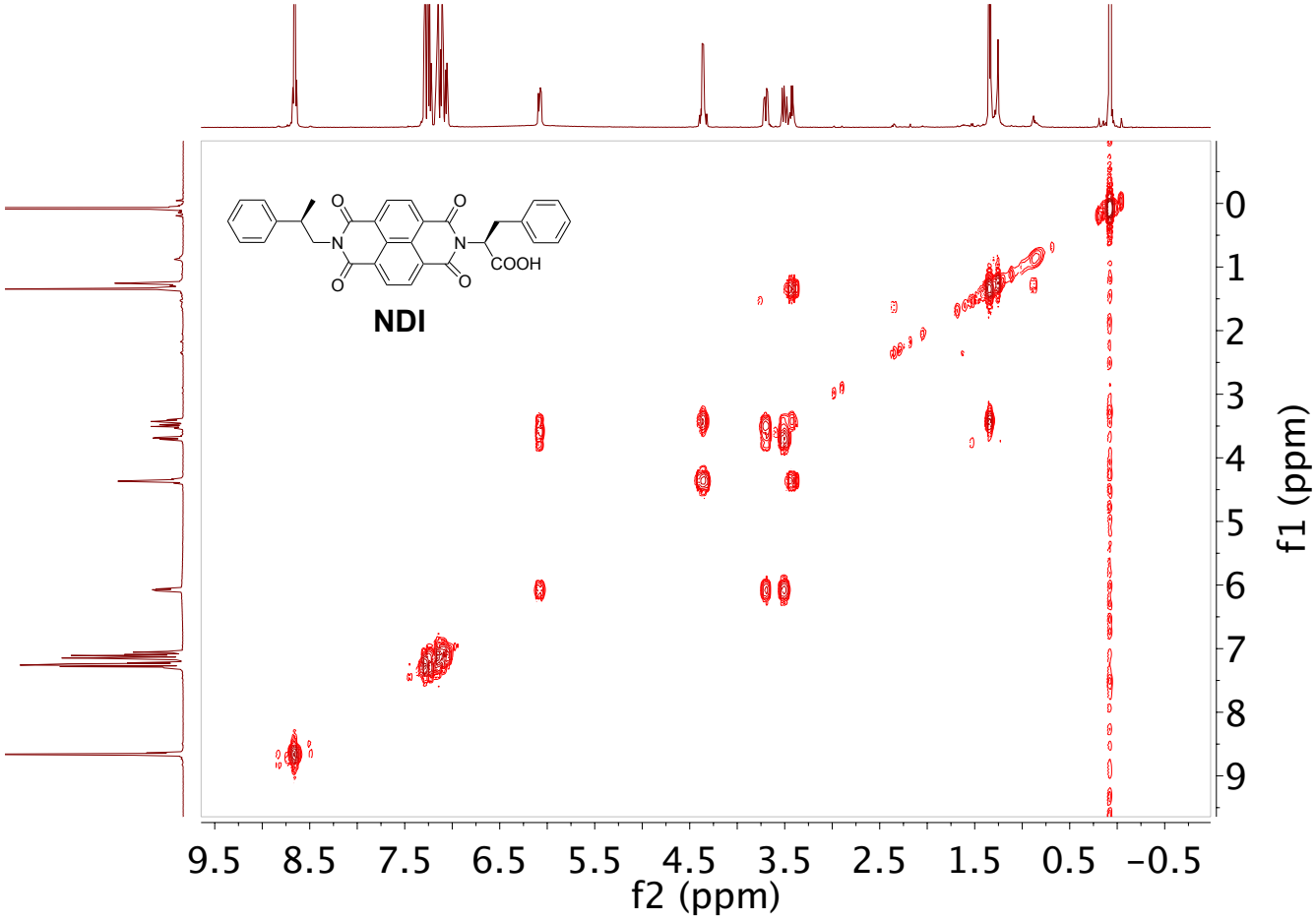
f1 (ppm)


NDI
COOH
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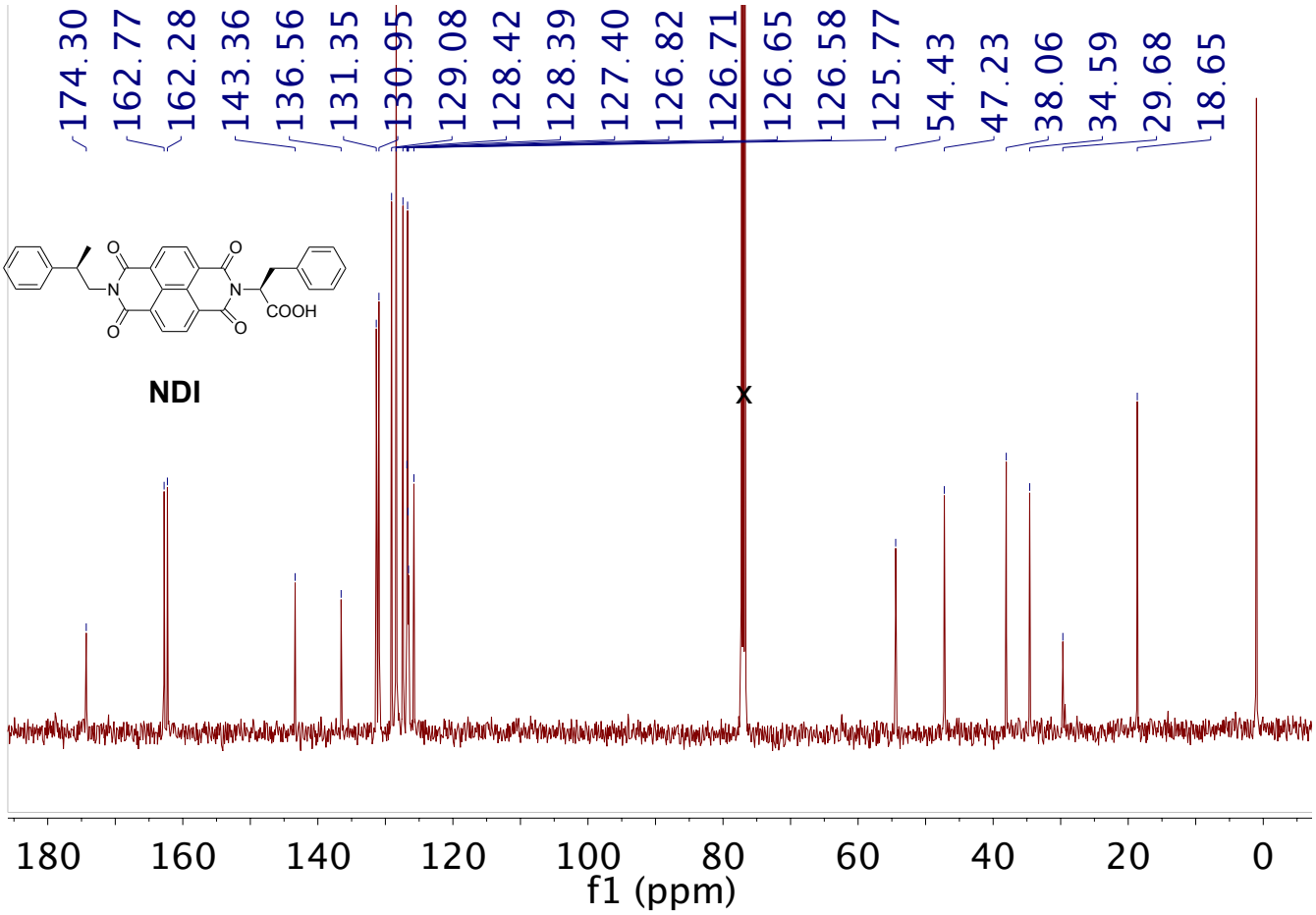
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)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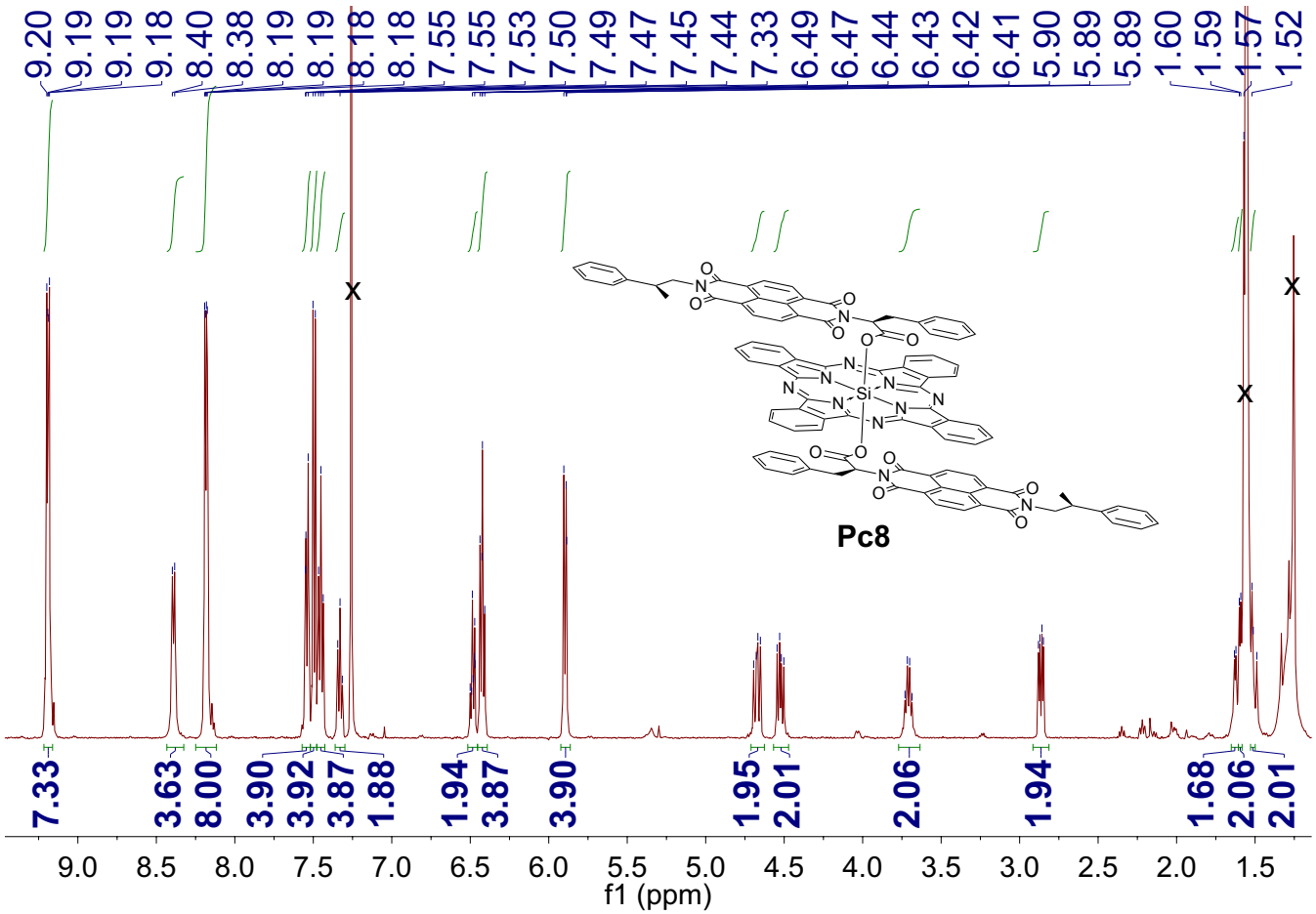
130.95
129.08
128.42
128.39
127.40
126.82
126.71
126.65
126.58
125.77
54.43
47.23
38.06
34.59
29.68
18.65
NDI
COOH
x
180 160 140 120 100 80 60 40 20 0
f1 (ppm)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7.33 3.63 8.00 3.90 3.92 3.87 1.88 1.94 3.87 3.90 1.95 2.01 2.06 1.94 1.68 2.06 2.01
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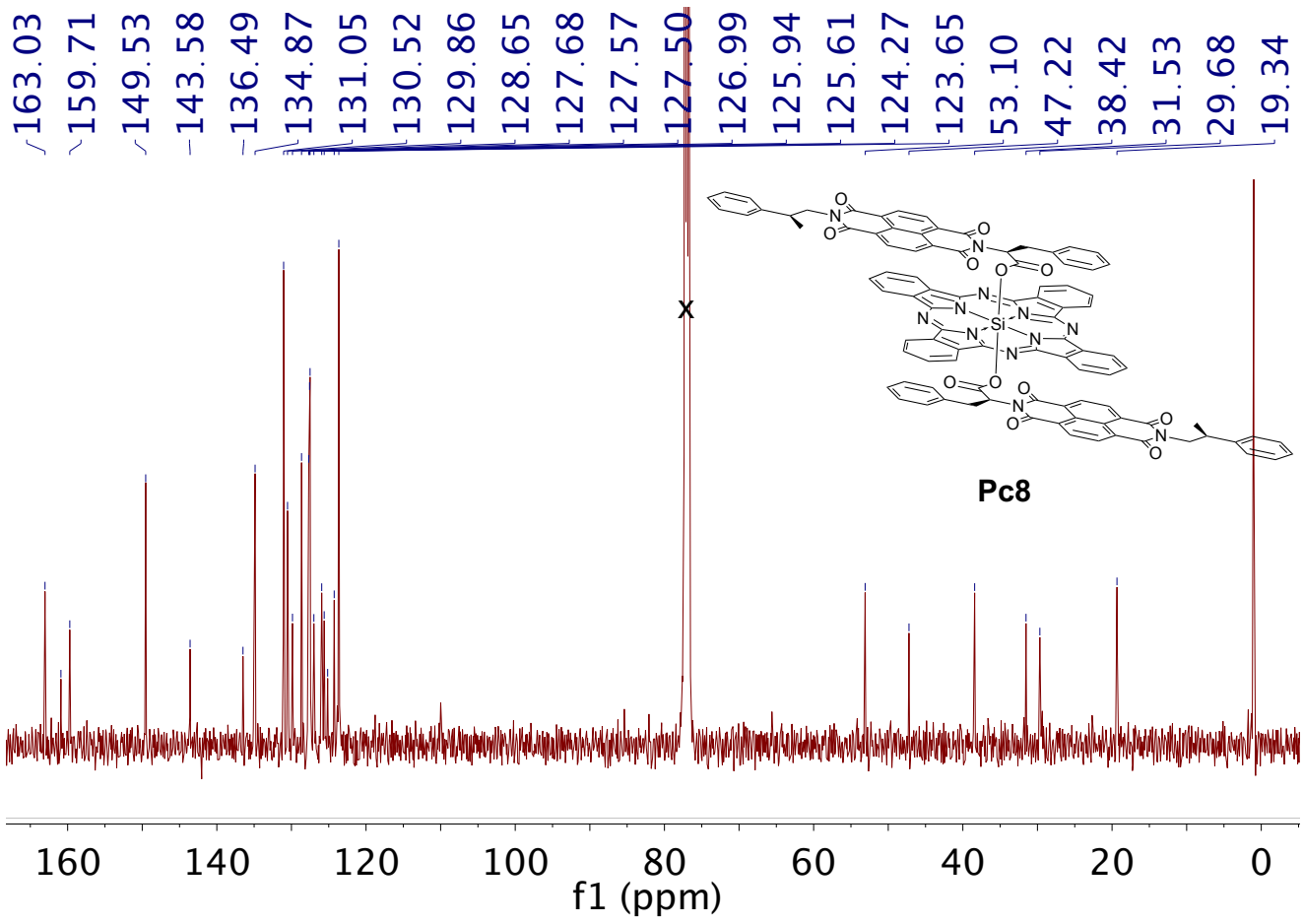
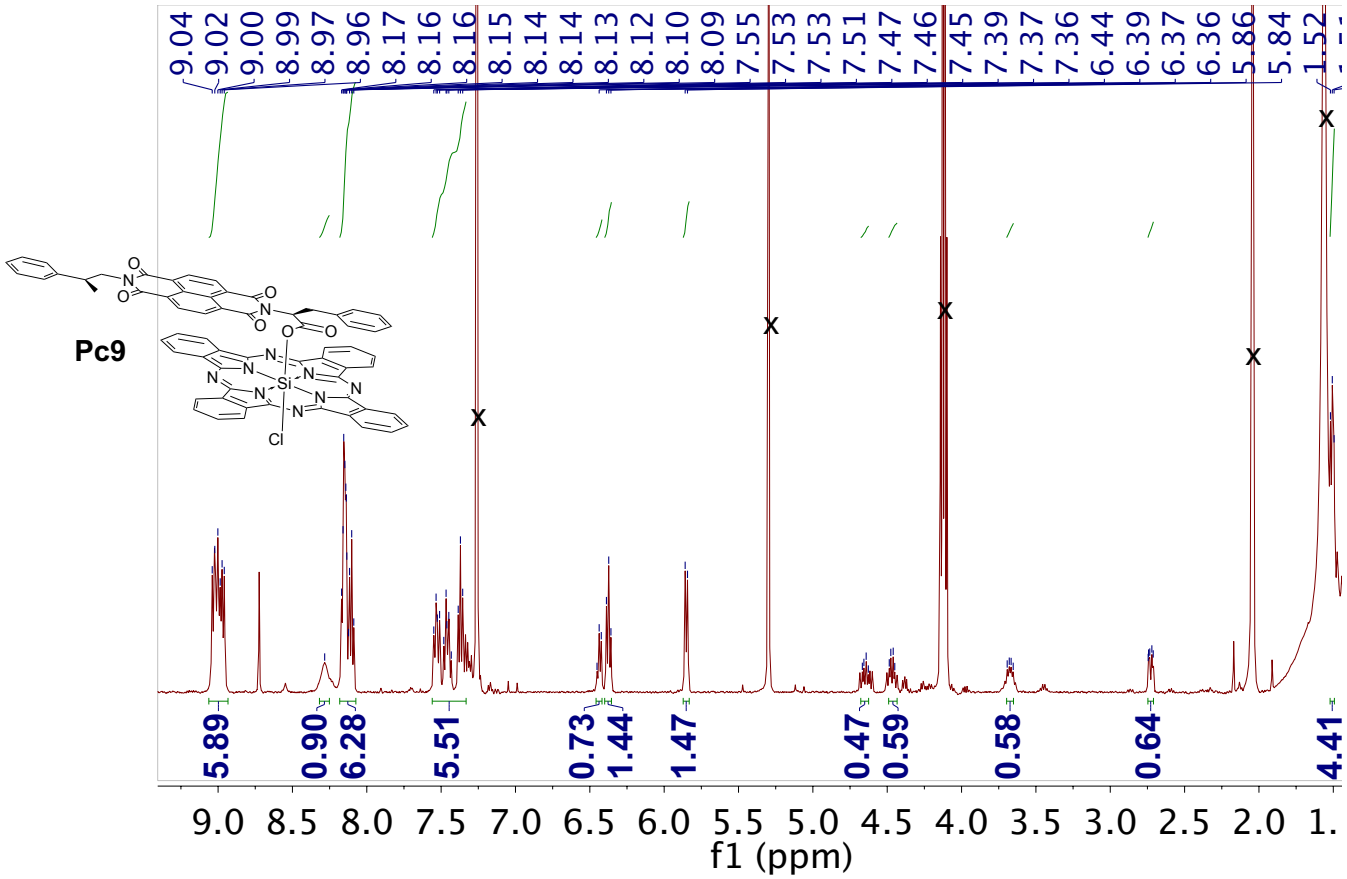
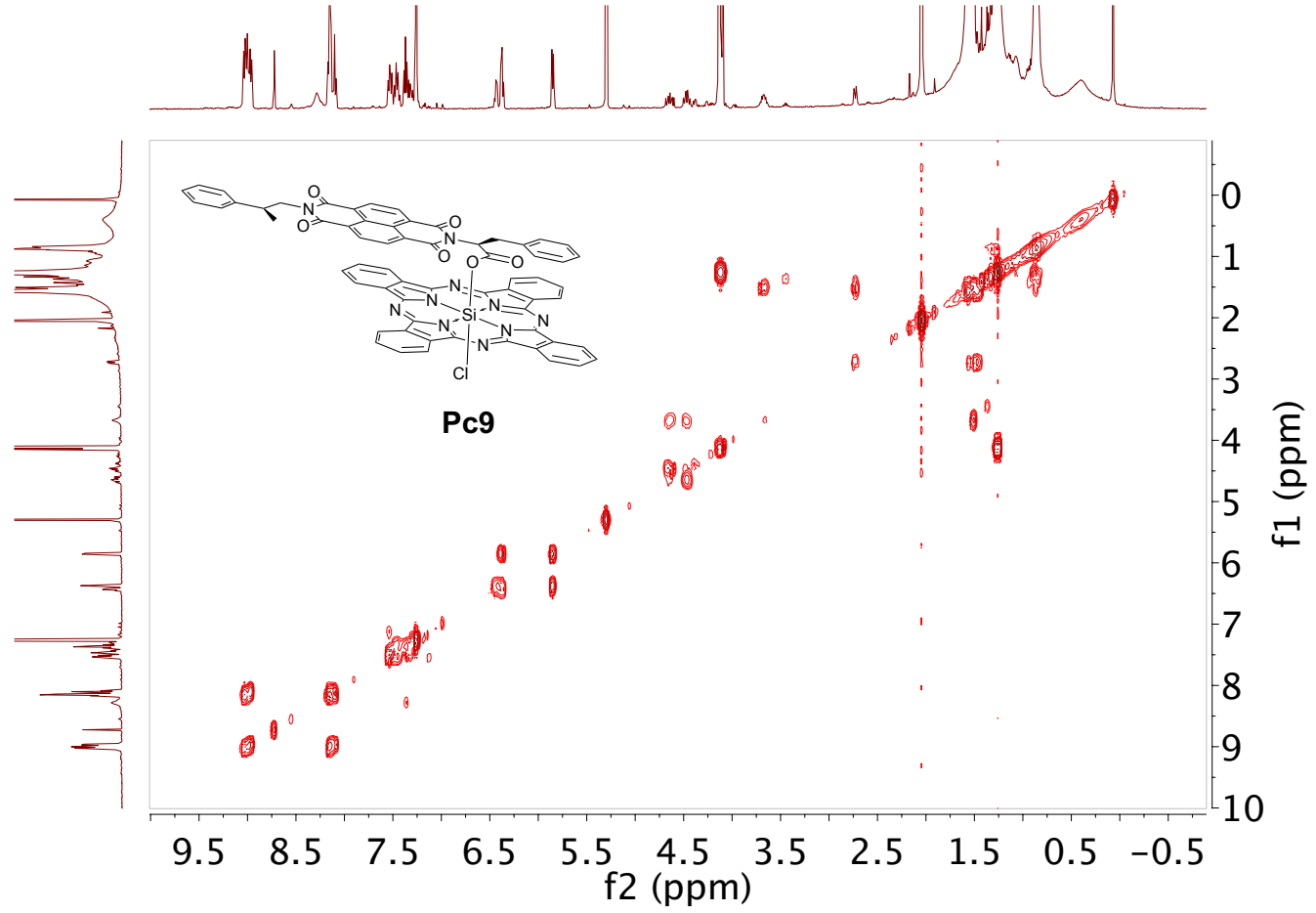
f1 (ppm)
Pc8


163.03 159.71 149.53 143.58 136.49 134.87 131.05 130.52 129.86 128.65 127.68 127.57 127.50 126.99 125.94 125.61 124.27 123.65 53.10 47.22 38.42 31.53 29.68 19.34
160 140 120 100 80 60 40 20 0
f1 (ppm)
Pc8


9.04 9.02 9.00 8.99 8.97 8.96 8.17 8.16 8.16 8.15 8.14 8.14 8.13 8.12 8.10 8.09 7.55 7.53 7.53 7.51 7.47 7.46 7.45 7.39 7.37 7.36 6.44 6.39 6.37 6.36 5.86 5.84 1.52
Pc9
5.89 0.90 6.28 5.51 0.73 1.44 1.47 0.47 0.59 0.58 0.64 4.41
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.
f1 (ppm)


Pc9
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f2 (ppm)
0 1 2 3 4 5 6 7 8 9 10
f1 (ppm)

Circular dichroism (CD), absorbance and fluorescence analyses

All the CD / UV-Vis spectra (Figures S1 – S5; molar extinction coefficients graphs are provided in Figure S15) were recorded in CH_2Cl_2 with a 1 cm quartz cuvette, and the background corresponding to solvent and cuvette's absorption was subtracted from subsequent measurements. The following parameters were used for CD and UV-Vis studies: wavelength range 250 – 800 nm, time-per-point 1 sec, monochromator bandwidth 2.5 nm, temperature 20 °C. Fluorescence spectra (Figures S6 – S14) were recorded in CH_2Cl_2 with a 1 cm fluorescence quartz cuvette. The excitation wavelengths for emission spectra were selected from the UV-Vis data, and the emission wavelengths for excitation spectra from emission ones. The parameters used in fluorescence studies were as following: wavelength range 300 – 800 nm, time-per-point 1 sec, monochromator bandwidth 12 nm, slit width 1 mm (bandpass 4.65 nm), PMU 1000 V, temperature 20 °C. The principal spectral properties of **Pcs1-9** are summarized in Table S1. According to the chiral exciton theory, an optically inactive chromophore that exhibits a negative CD signal corresponding to its electronic absorption develops surrounding asymmetric fields, determining the molecule to be right handed.[5] Based on this theory, the **Pcs4**, **5**, **8** and **9**, which display a positive CD signal at long wavelengths, are left-handed, whereas the ones showing negative signals are right-handed.

Table S1. Spectral characteristics as well as molar extinction coefficients (ε) of **Pcs1-9**.

product name	λ_{max} from Soret-band (nm)	λ_{max} from Q-band (nm)	λ_{max} in emission[a] (nm)	Stokes shift[b] (nm)	molar extinction coefficient, ε (L mol^{-1} cm^{-1})
Pc1	348	688	693	5	234,000 ± 5560
Pc2	355	682	683	1	60,000 ± 1920
Pc3	360	688	693	5	259,000 ± 1370
Pc4	354	676	677	1	24,600± 300
Pc5	358	685	690	5	74,000 ± 610
Pc6	357	678	679	1	3,400 ± 190
Pc7	360	686	693	7	62,000 ± 200
Pc8	363	695; 626	673	n/a[c]	115,000 ± 3320
Pc9	359	684	671	-	50,000 ± 3500

[a]λ_{max} corresponding to the Q-band region from the UV-Vis spectra (excitation wavelengths).

[b]The Stokes shifts were determined using the longest wavelength in the emission spectra and its corresponding λ_{max} from the Q-band region.

[c]In this case, the Stokes shift could not be calculated due the fluorescence quenching nature of the axial ligand NDI which influences the emission at λ = 695 nm.

The emission spectra given below are shown from the wavelengths longer than the excitation wavelengths; note: the Stokes shifts as provided in Table S1.

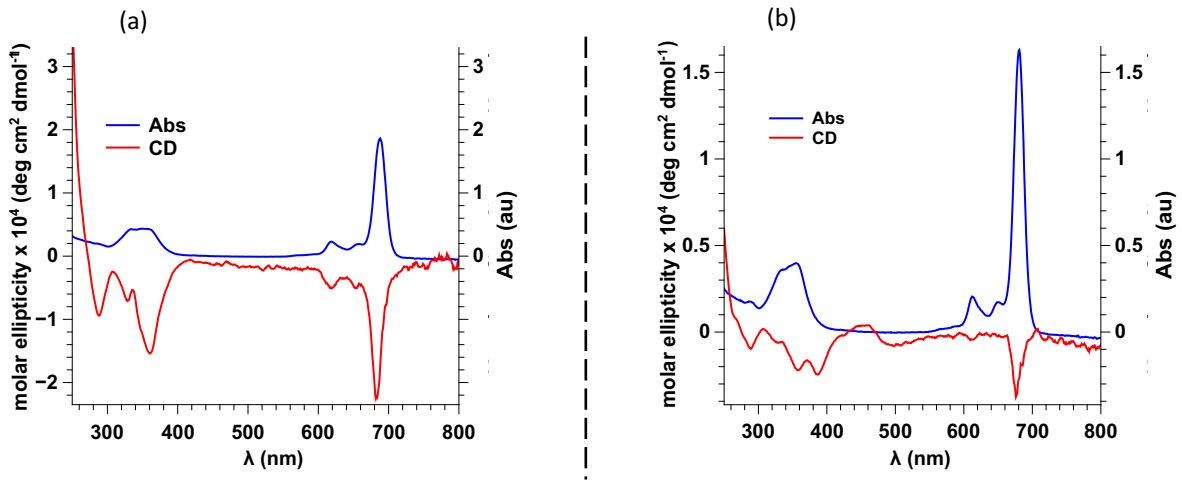


Figure S1. (a) Overlaid CD and UV-Vis spectra of **Pc1**. (b) Overlaid CD and UV-Vis spectra of **Pc2**.

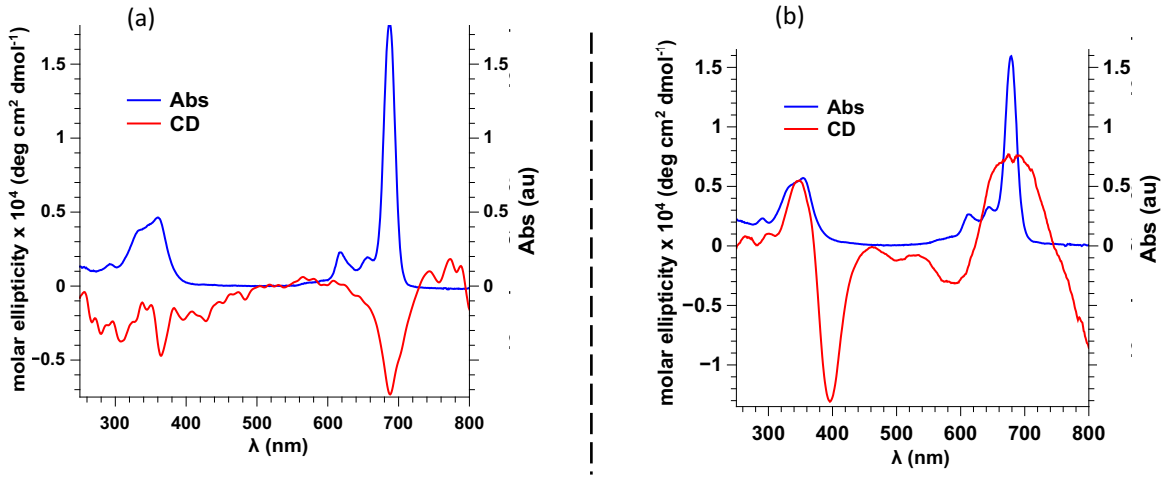


Figure S2. (a) Overlaid CD and UV-Vis spectra of **Pc3**. (b) Overlaid CD and UV-Vis spectra of **Pc4**.

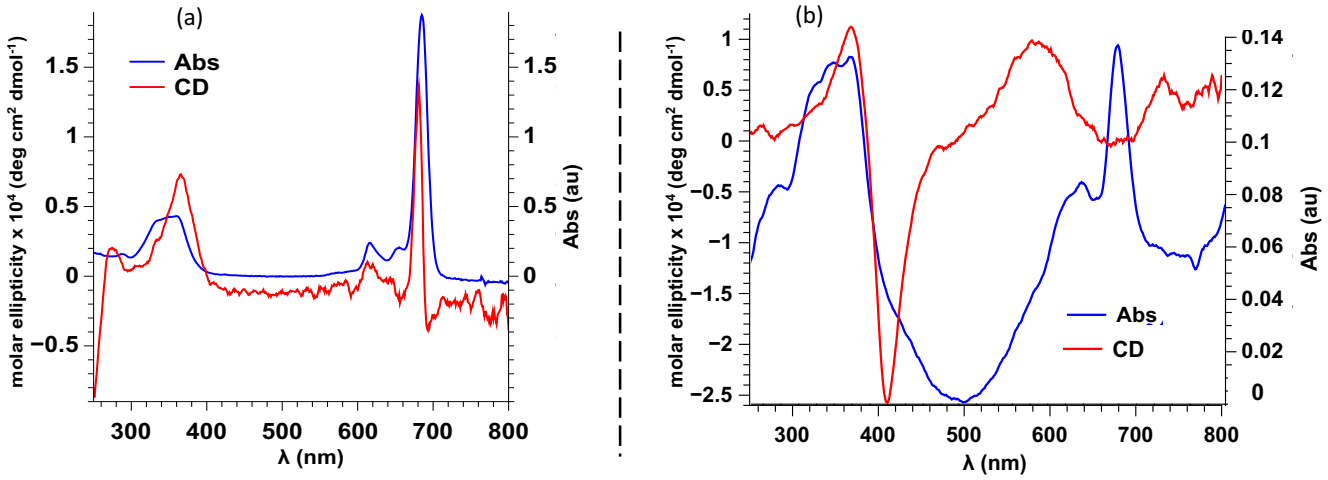


Figure S3. (a) Overlaid CD and UV-Vis spectra of **Pc5**. (b) Overlaid CD and UV-Vis spectra of **Pc6**.

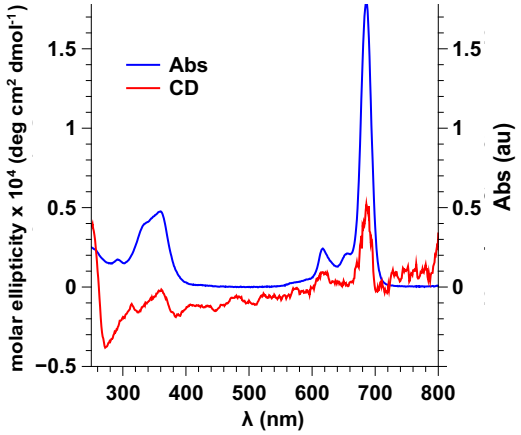


Figure S4. Overlaid CD and UV-Vis spectra of **Pc7**.

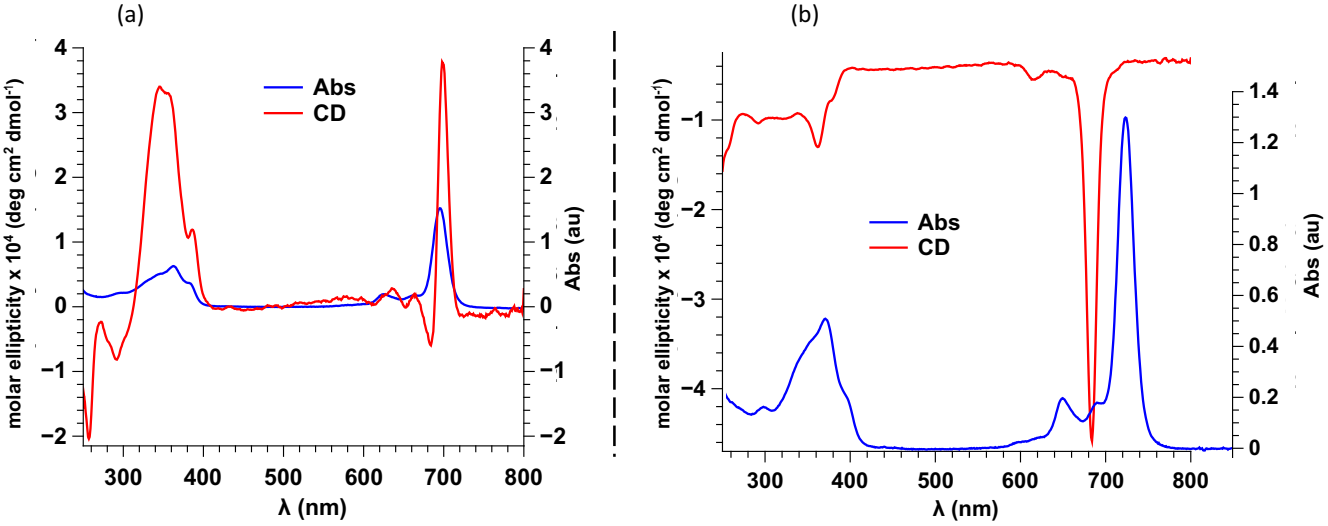


Figure S5. (a) Overlaid CD and UV-Vis spectra of **Pc8**. (b) Overlaid CD and UV-Vis spectra of **Pc9**.

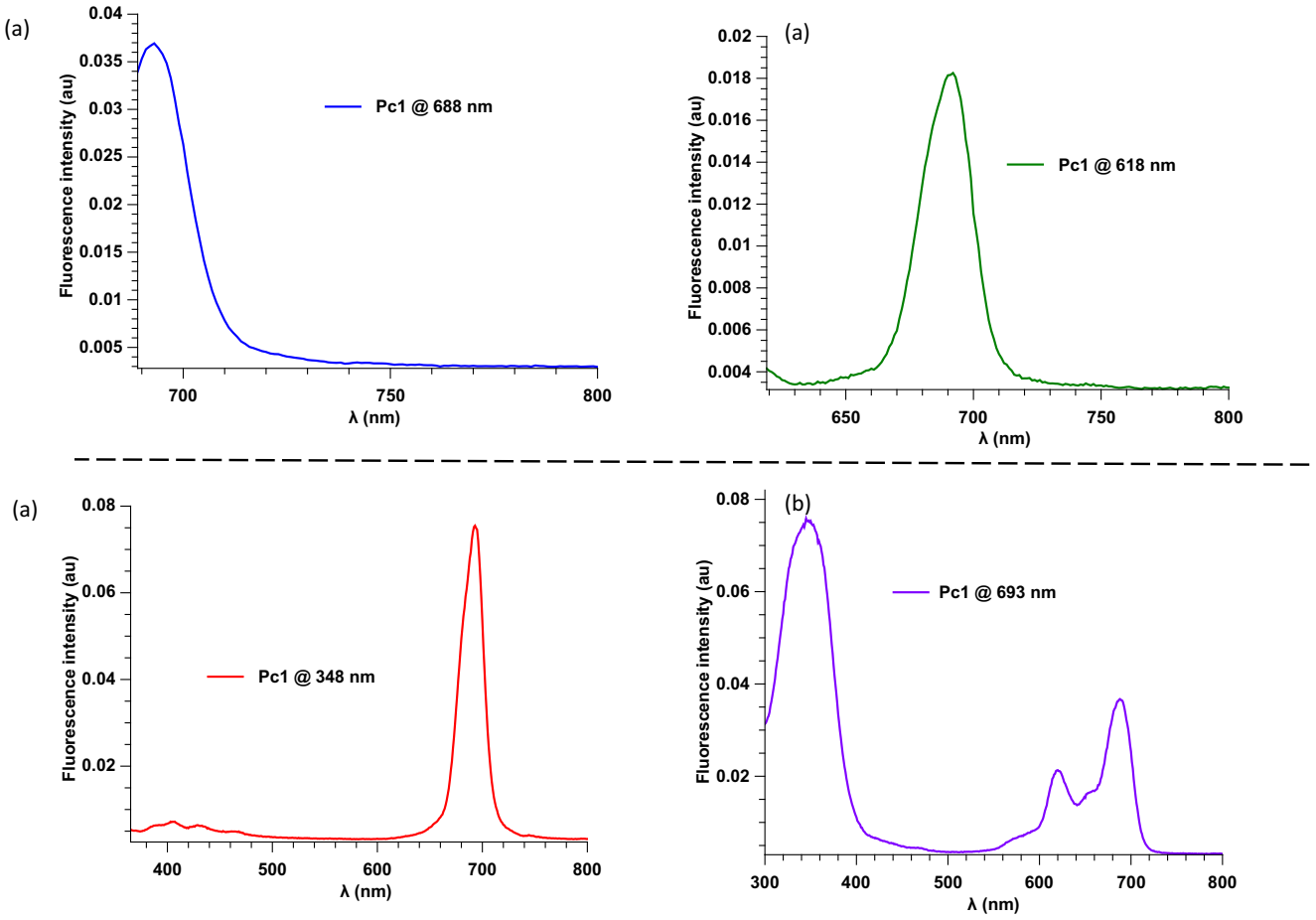


Figure S6. (a) Emission spectra of **Pc1**. (b) Excitation spectrum of **Pc1**. The excitation / emission wavelengths are provided in the legend.

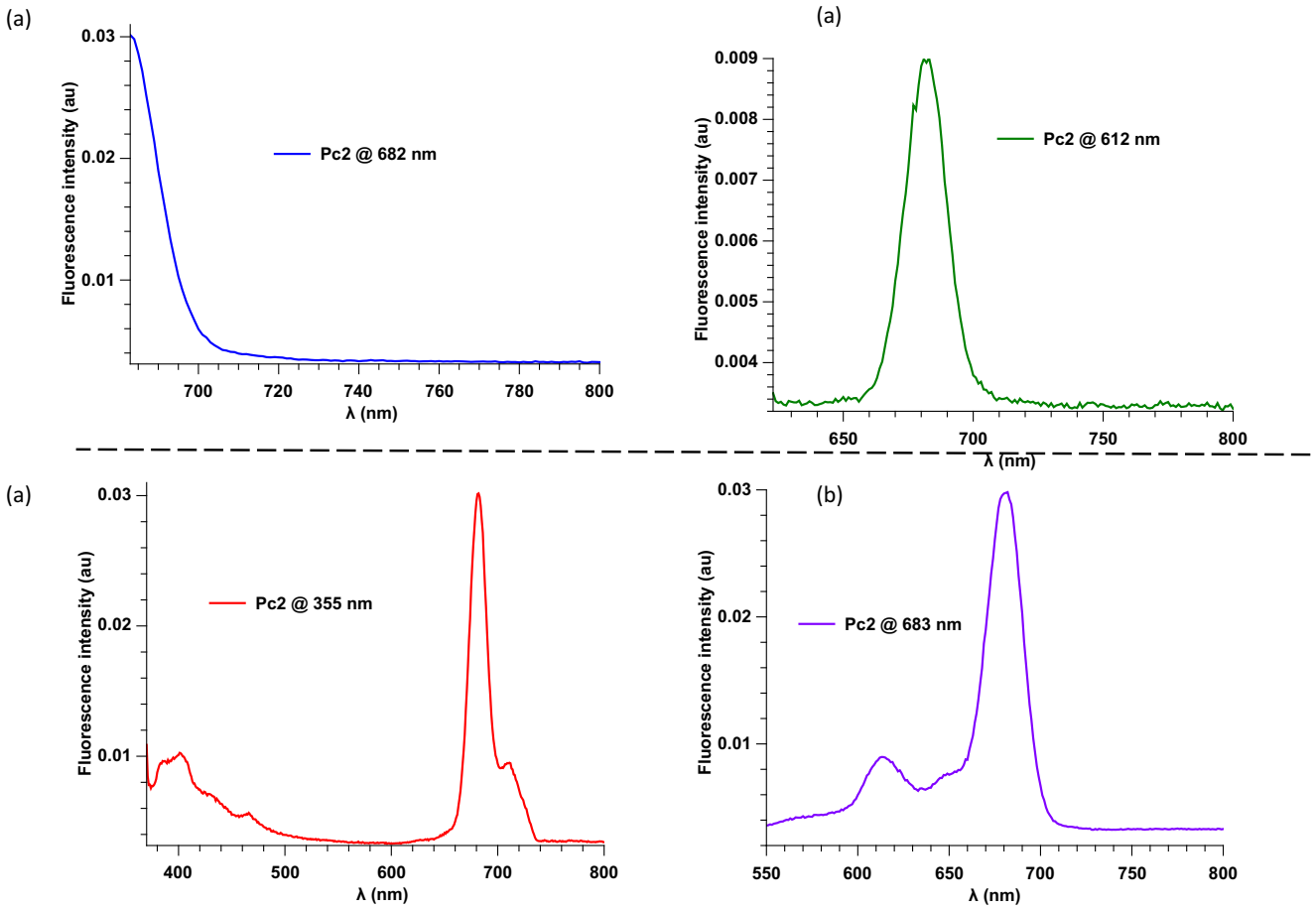


Figure S7. (a) Emission spectra of **Pc2**. (b) Excitation spectrum of **Pc2**. The excitation / emission wavelengths are provided in the legend.

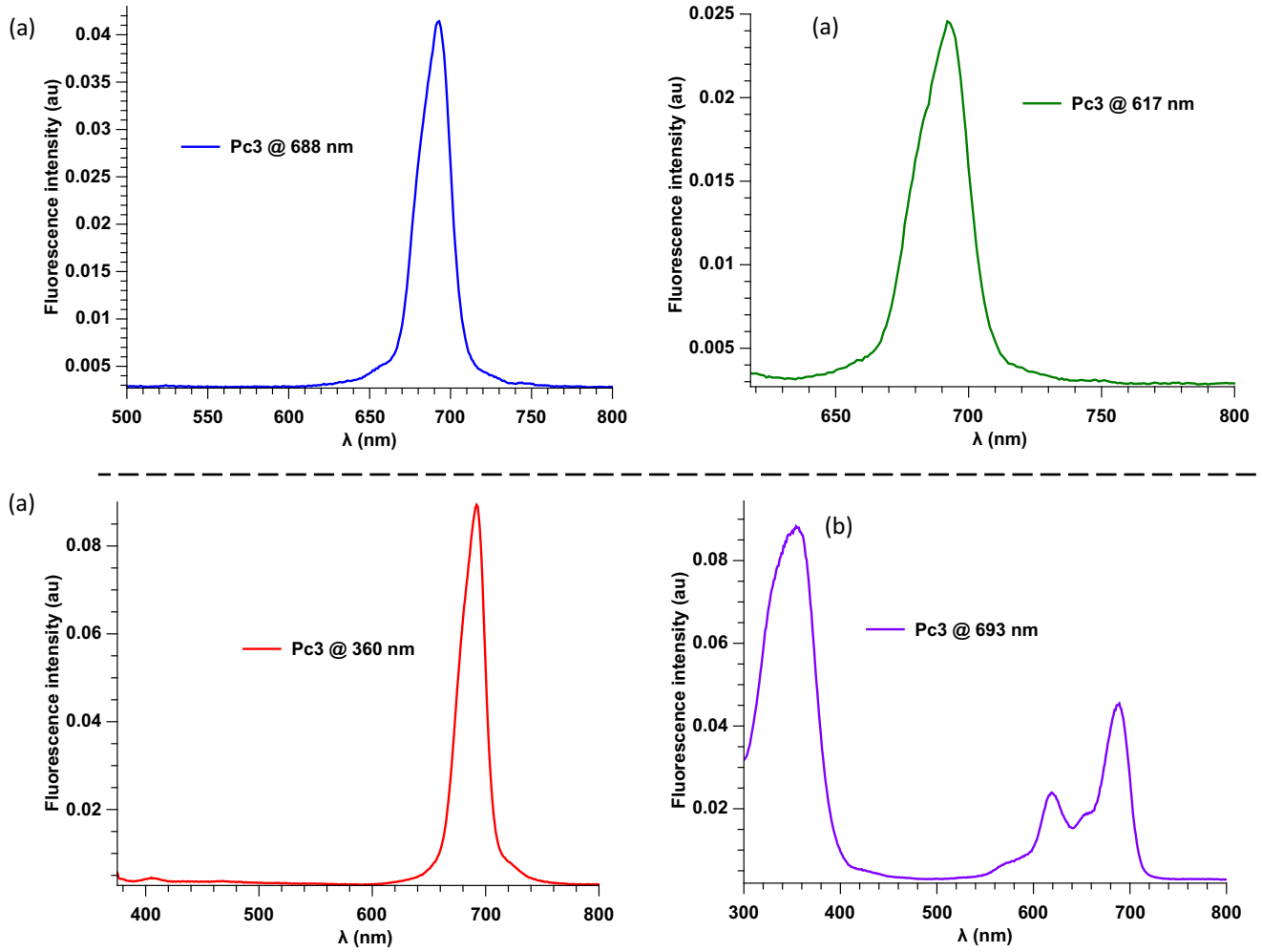


Figure S8. (a) Emission spectra of **Pc3**. (b) Excitation spectrum of **Pc3**. The excitation / emission wavelengths are provided in the legend.

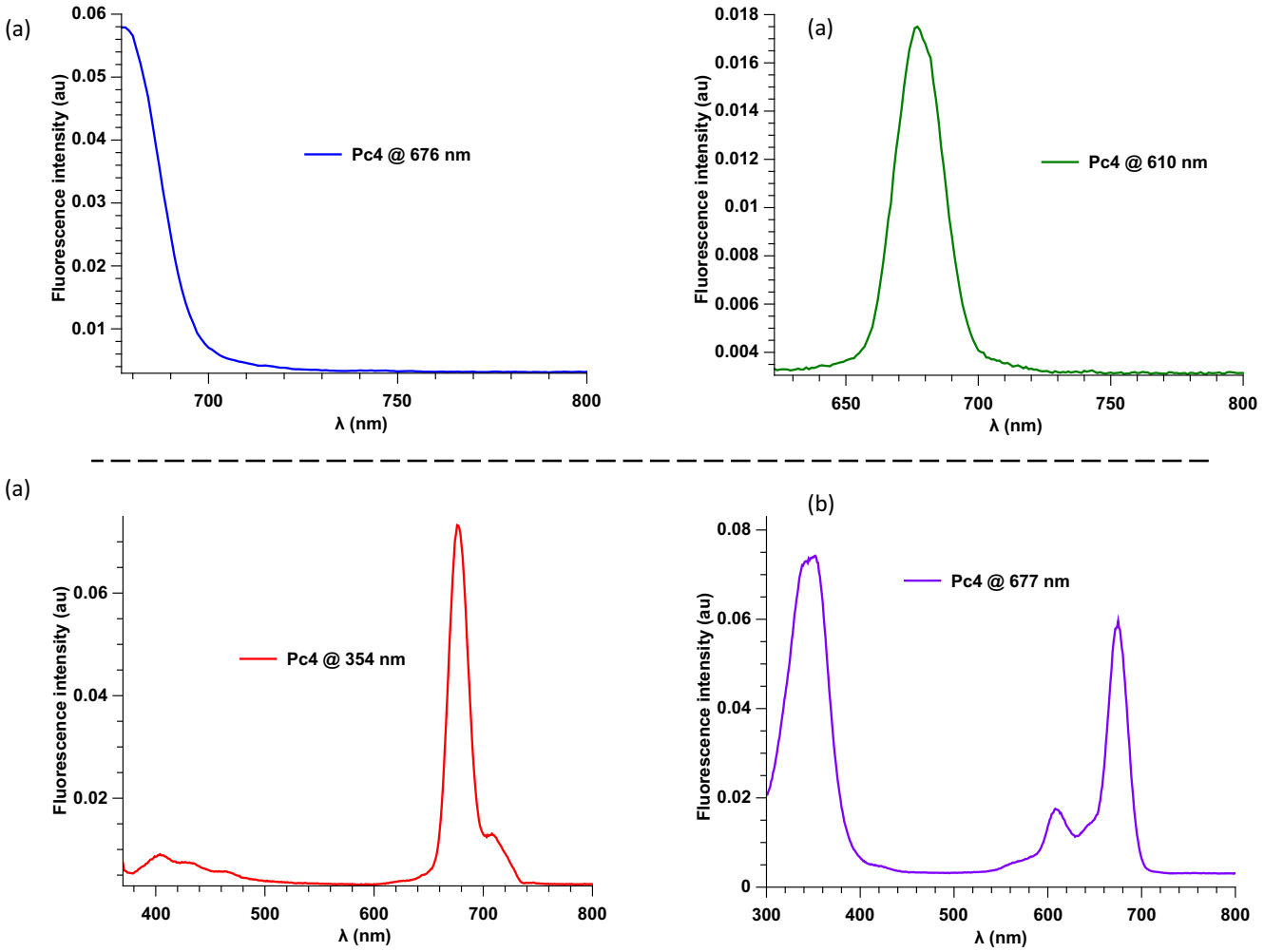


Figure S9. (a) Emission spectra of **Pc4**. (b) Excitation spectrum of **Pc4**. The excitation / emission wavelengths are provided in the legend.

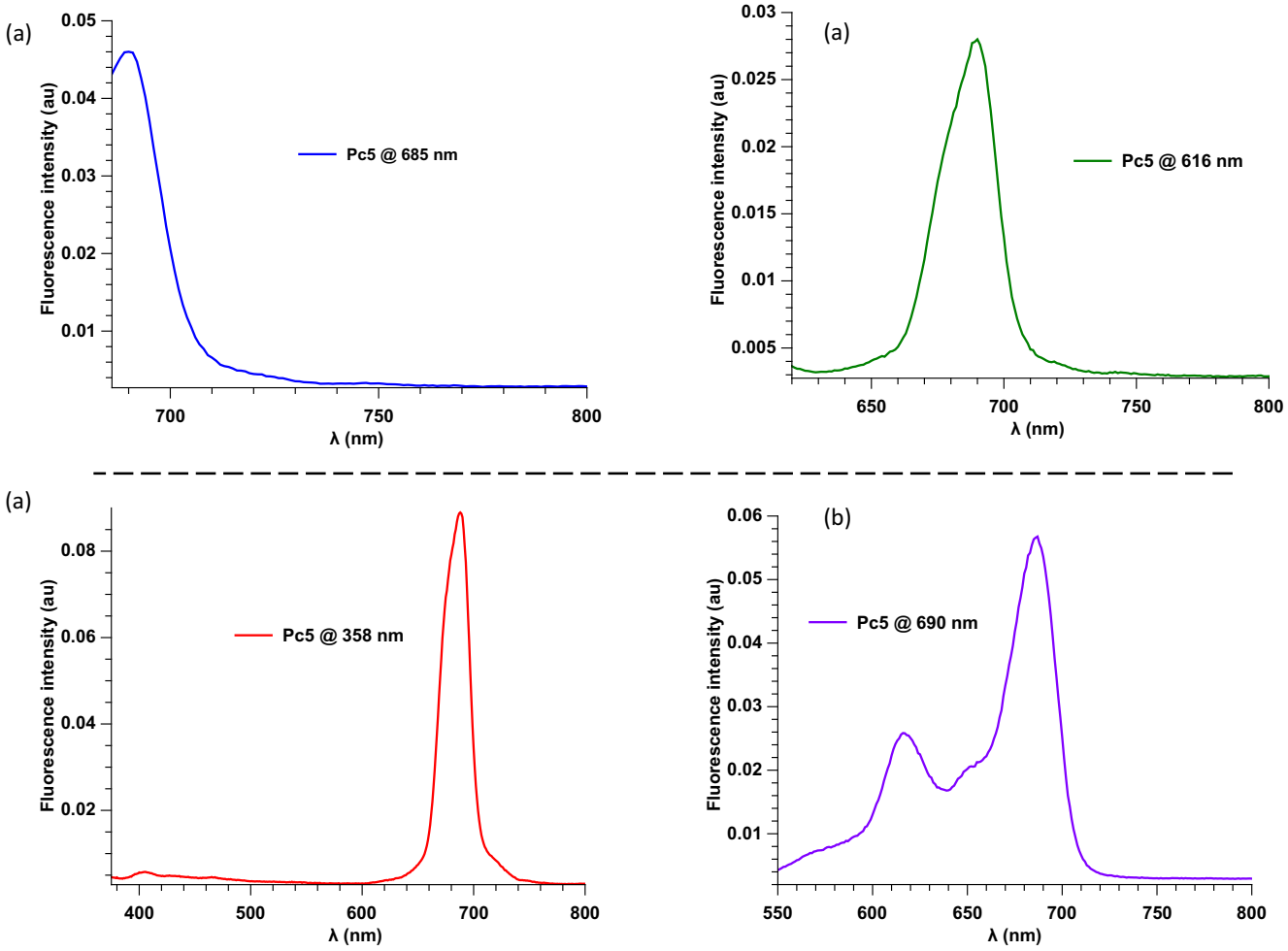


Figure S10. (a) Emission spectra of **Pc5**. (b) Excitation spectrum of **Pc5**. The excitation / emission wavelengths are provided in the legend.

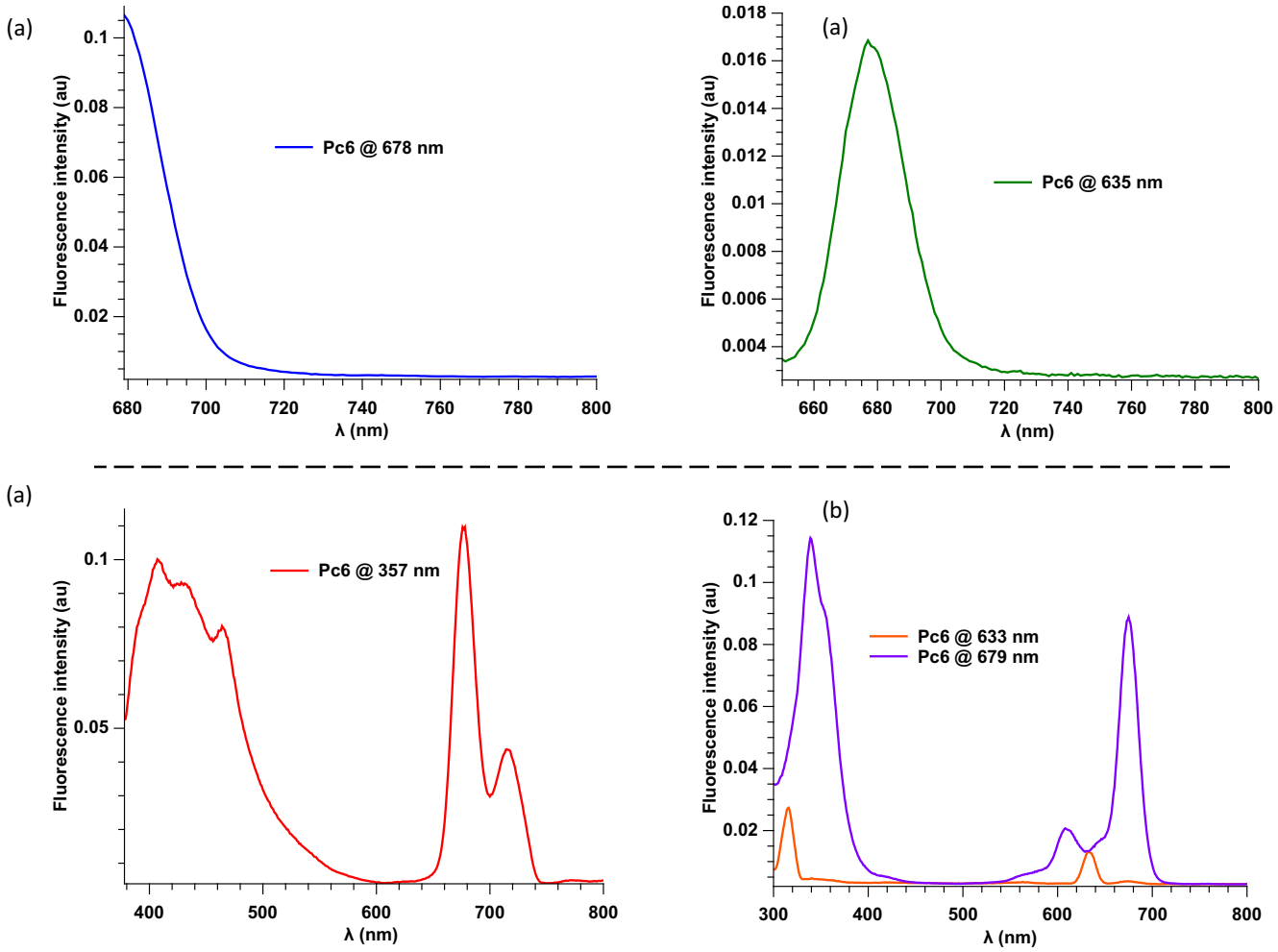


Figure S11. (a) Emission spectra of **Pc6**. (b) Overlaid excitation spectra of **Pc6**. The excitation / emission wavelengths are provided in the legend.

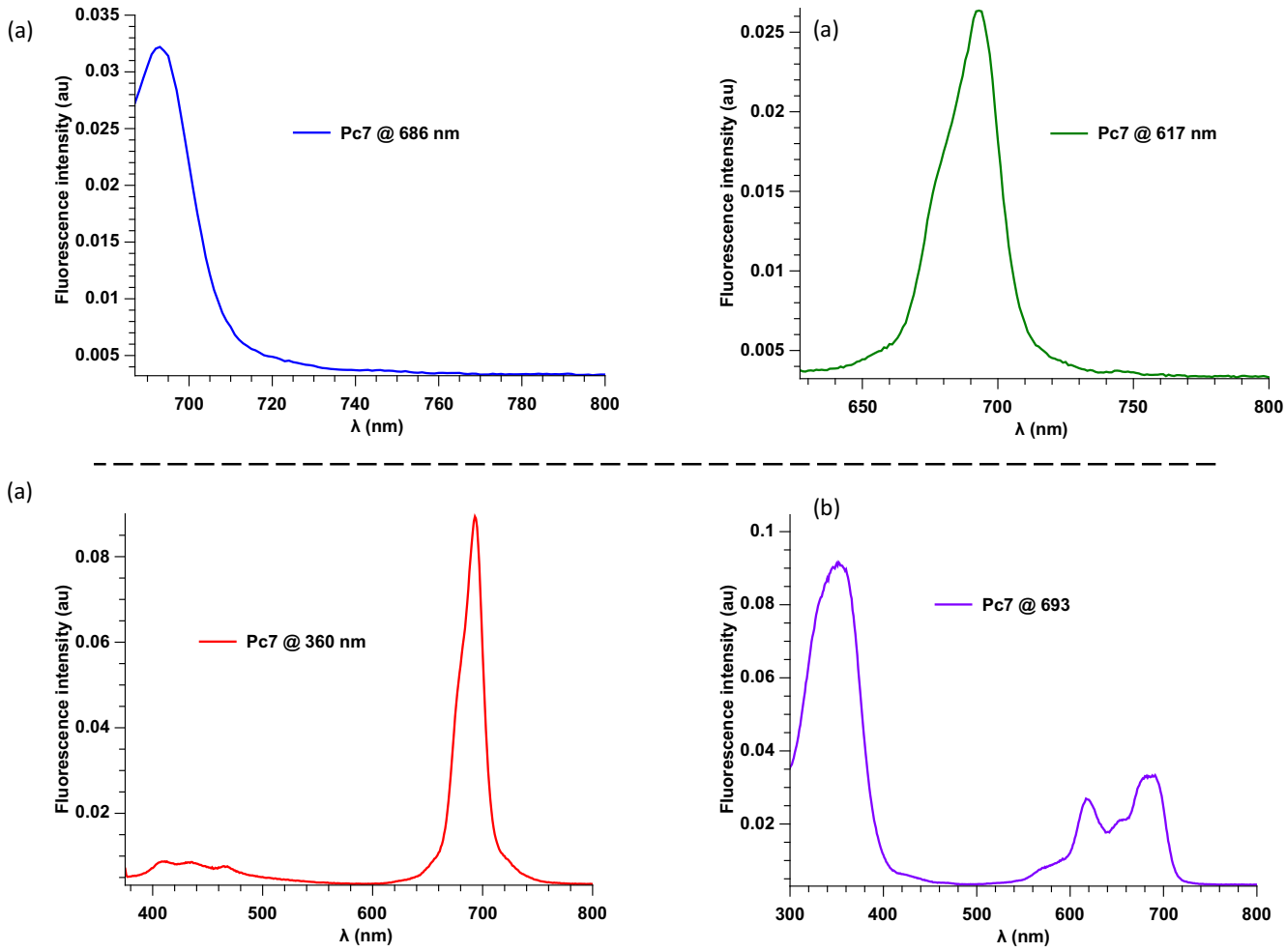


Figure S12. (a) Emission spectra of **Pc7**. (b) Excitation spectrum of **Pc7**. The excitation / emission wavelengths are provided in the legend.

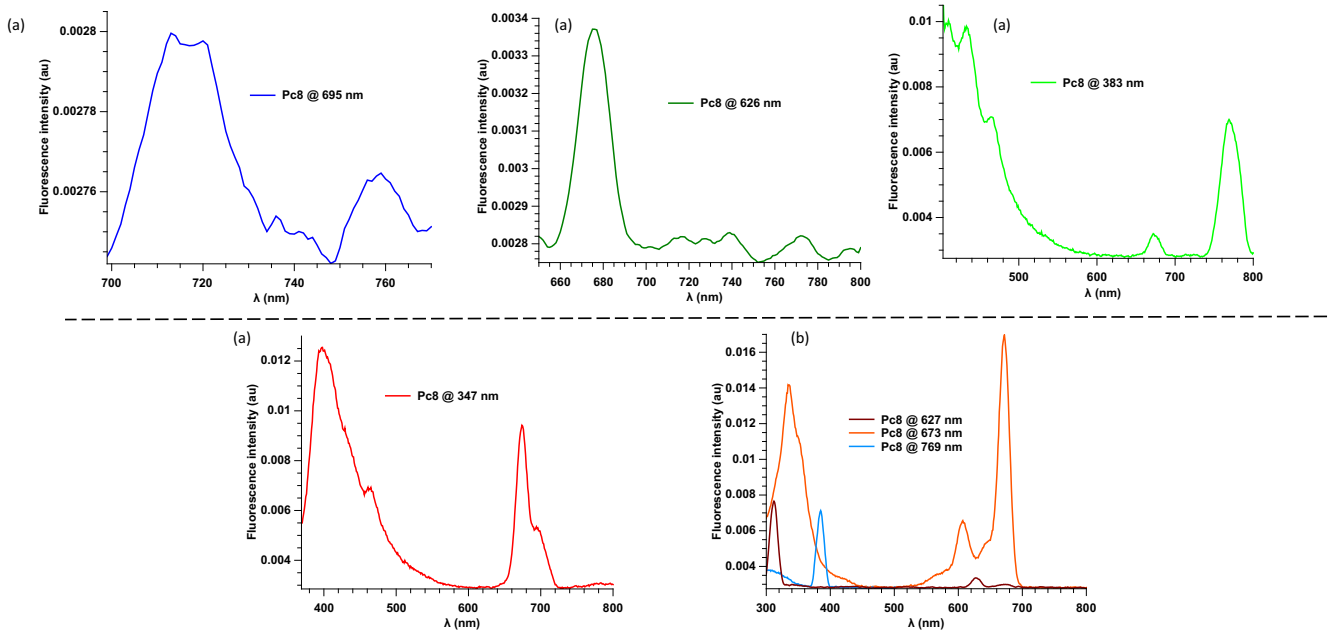
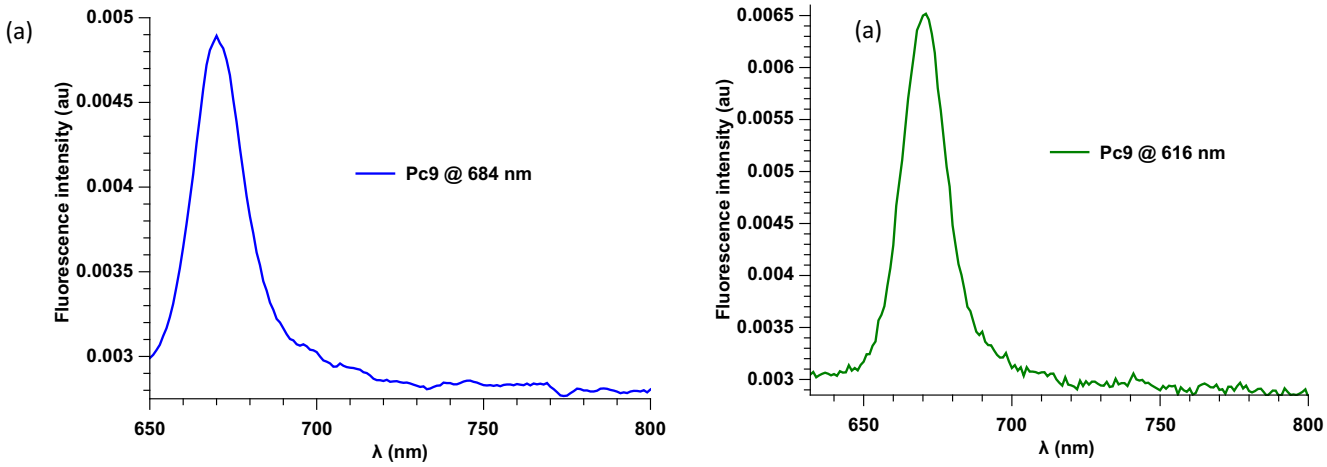


Figure S13. (a) Emission spectra of **Pc8**. (b) Excitation spectrum of **Pc8**. The excitation / emission wavelengths are provided in the legend.



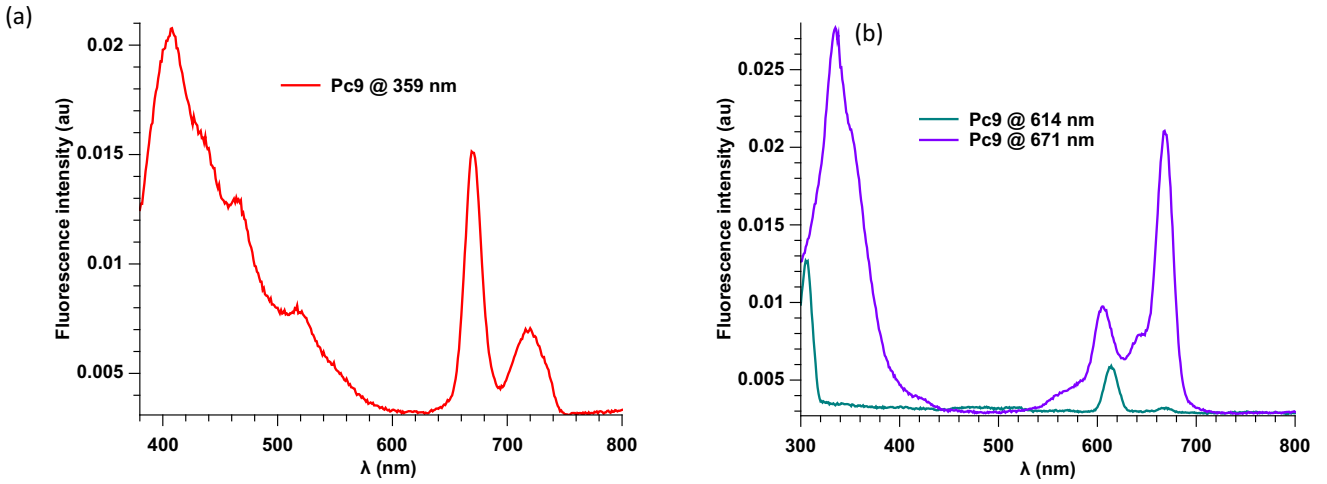


Figure S14. (a) Emission spectra of **Pc9**. (b) Excitation spectrum of **Pc9**. The excitation / emission wavelengths are provided in the legend.

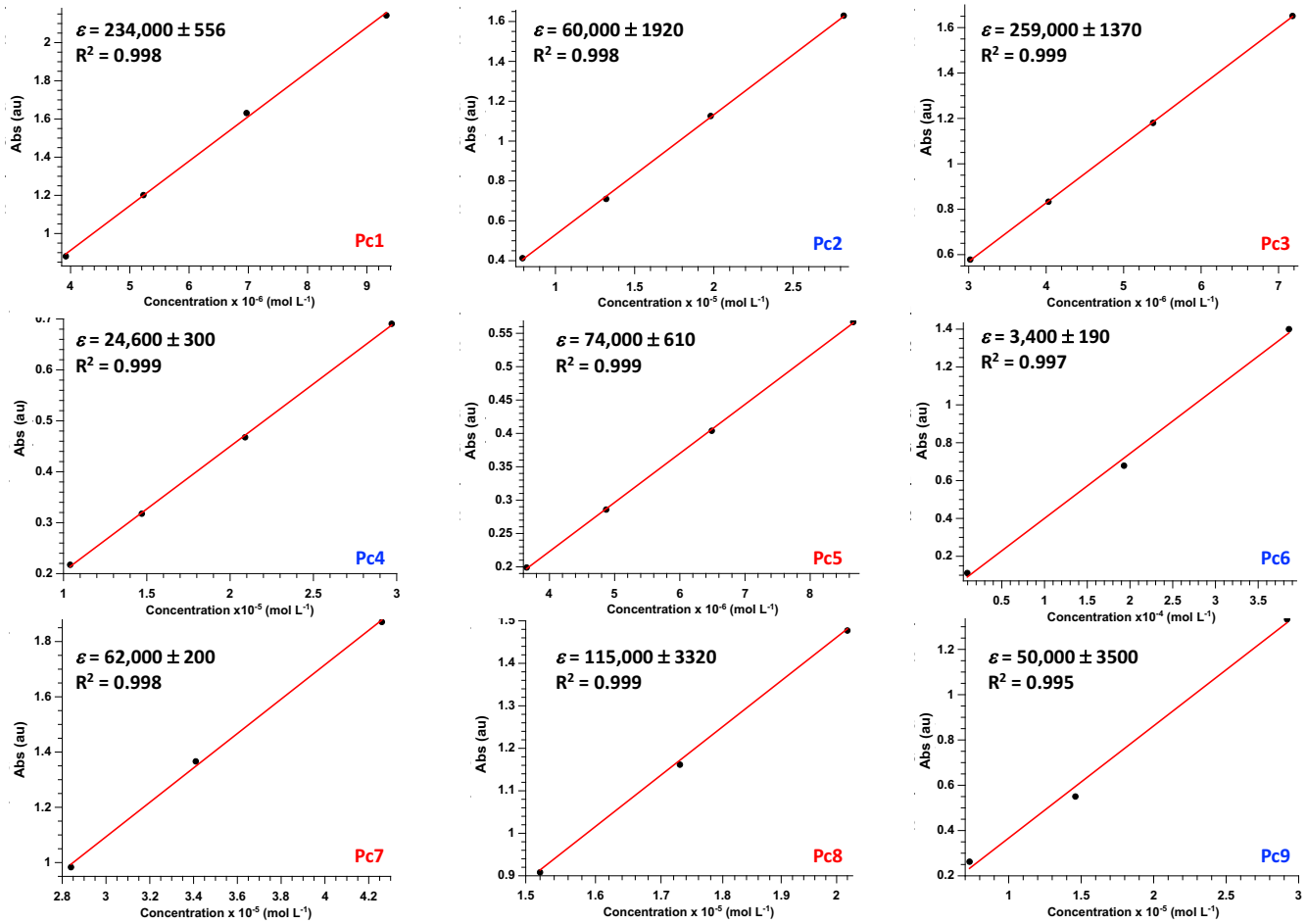


Figure S15. Plots of the absorbance data *versus* concentration used for molar extinction coefficients calculation. A first order equation was applied to these and the values are provided on the top left corner of each graph as well as in Table S1. The Si-Pc-di-substituted derivatives are red-coded, and the mono-analogues are blue-coded.

Quantum yield determination (Φ_f)

The quantum yields of di-substituted **Pcs1**, **3**, **7** and the mono-derivative **Pc9** have been calculated using Rhodamine 800 as the reference. The quantum yield of rhodamine 800 in methanol reported in the literature is 0.16.[6] The quantum yields have been determined according to the general procedure.[7] We have attempted to calculate the quantum yields of the mono-substituted Si-Pcs, but failed due to the aggregation issue.

X-ray analysis

Crystallographic data

Intensity data were collected at 150 K on a Rigaku SuperNova, Dual, EosS2, using CuKα radiation (λ = 1.54184 Å). **(Pc5)** $C_{50}H_{34}N_8O_4Si$, M = 838.94, $P2_12_12_1$, *a* = 8.45760(10) Å, *b* = 20.7860(3) Å, *c* = 22.1729(3) Å, *V* = 3897.99(9) Å^3, *Z* = 4, μ = 1.035 mm^{-1}, unique reflections = 7725 [R(int) = 0.0460], R_1 = 0.0356, wR_2 = 0.0796 [I>2σ(I)], R_1 = 0.0429, wR_2 = 0.0825 (all data). CCDC 1578829. **(Pc8)** $C_{96}H_{62}N_{12}O_{12}Si$, M = 1603.66, $P4_32_12$, *a* = 12.3595(5) Å, *c* = 50.594(4) Å, *V* = 7728.6(9) Å^3, *Z* = 4, μ = 0.899 mm^{-1}, unique reflections = 6850 [R(int) = 0.2215], R_1 = 0.1087, wR_2 = 0.2389 [I>2σ(I)], R_1 = 0.2294, wR_2 = 0.3396 (all data). CCDC 1578830. See https://www.ccdc.cam.ac.uk/structures/ for crystallographic data in the .cif format.

The presence of weak C-H···O=C interactions (2.98 Å, 136.5°) between the adjacent NDI units within the structure of **Pc8** (described in the manuscript) is illustrated in Figure S16.

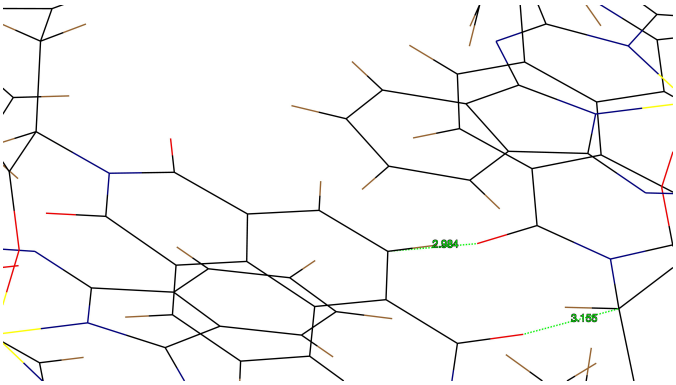


Figure S16. Image showing the C-H···O=C interactions between adjacent NDI units of **Pc8**.

Single crystals, suitable for X-ray diffraction analysis, of **Pc5** have been also obtained by slow evaporation of a chloroform solution. The molecule crystallizes in a $P2_12_12_1$ group space, with the carboxylates moieties arranged in *trans* geometry in respect to each other (Figure S17). There are aromatic π-π interactions between the axial ligand and Pc core, assembling into an extended stack; the interplanar separation is 3.351 Å. Moreover, the different columns forming these stacks are arranged in a herringbone-like fashion as illustrated in Figure S18.

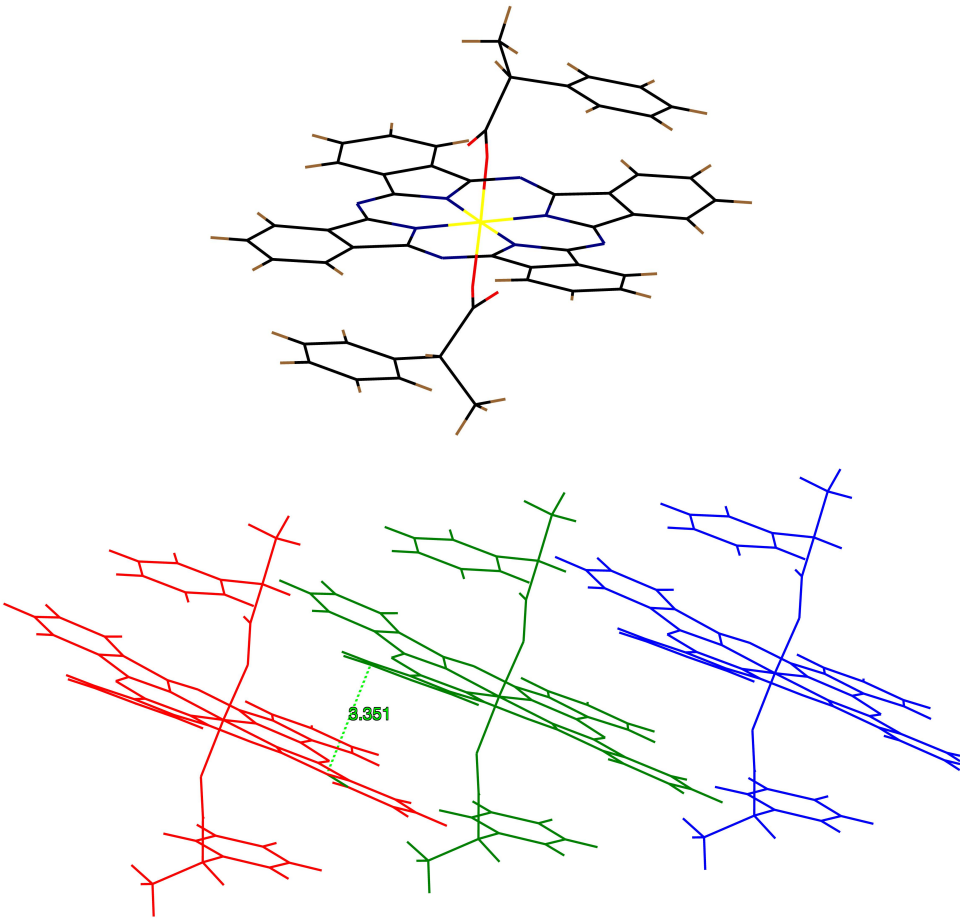


Figure S17. (top) Crystal structure of **Pc5**. The atoms are color-coded as following: Si – yellow, C – black, N – blue, O – red, H – brown. (bottom) Fragment of an infinite aromatic π-π stacking in the crystal packing of **Pc5** showing the interplanar separation.

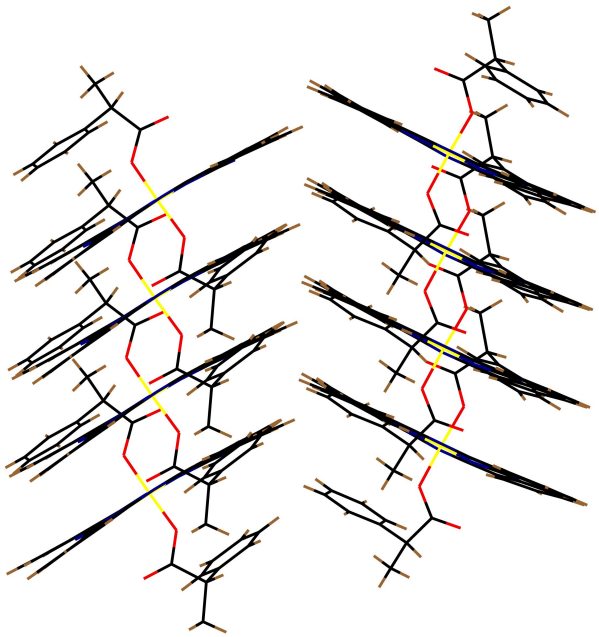


Figure S18. The herringbone-like arrangement of the infinite stacking of **Pc5**.

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